INTERNATIONAL ATOMIC WEIGHTS, 1957

[Reprinted (with omission of actinides) from the Report of the Commission on Atomic Weights in the Comptes rendus *of the 19th Conference of the International Union of Pure and Applied Chemistry, 1957.]*

Name	Symbol	Atomic weight	Name	Symbol	Atomic weight
Aluminium	Al	26·98	Molybdenum	Mo	95·95
Antimony	Sb	121·76	Neodymium	Nd	144·27
Argon	Ar	39·944	Neon	Ne	20·183
Arsenic	As	74·91	Nickel	Ni	58·71
Barium	Ba	137·36	Niobium	Nb	92·91
Beryllium	Be	9·013	Nitrogen	N	14·008
Bismuth	Bi	209·00	Osmium	Os	190·2
Boron	B	10·82	Oxygen	O	16
Bromine	Br	79·916	Palladium	Pd	106·4
Cadmium	Cd	112·41	Phosphorus	P	30·975
Cæsium	Cs	132·91	Platinum	Pt	195·09
Calcium	Ca	40·08	Potassium	K	39·100
Carbon	C	12·011	Praseodymium	Pr	140·92
Cerium	Ce	140·13	Rhenium	Re	186·22
Chlorine	Cl	35·457	Rhodium	Rh	102·91
Chromium	Cr	52·01	Rubidium	Rb	85·48
Cobalt	Co	58·94	Ruthenium	Ru	101·1
Copper	Cu	63·54	Samarium	Sm	150·35
Dysprosium	Dy	162·51	Scandium	Sc	44·96
Erbium	Er	167·27	Selenium	Se	78·96
Europium	Eu	152·0	Silicon	Si	28·09
Fluorine	F	19·00	Silver	Ag	107·880
Gadolinium	Gd	157·26	Sodium	Na	22·991
Gallium	Ga	69·72	Strontium	Sr	87·63
Germanium	Ge	72·60	Sulphur	S	32·066
Gold	Au	197·0	Tantalum	Ta	180·95
Hafnium	Hf	178·50	Tellurium	Te	127·61
Helium	He	4·003	Terbium	Tb	158·93
Holmium	Ho	164·94	Thallium	Tl	204·39
Hydrogen	H	1·0080	Thorium	Th	232·05
Indium	In	114·82	Thulium	Tm	168·94
Iodine	I	126·91	Tin	Sn	118·70
Iridium	Ir	192·2	Titanium	Ti	47·90
Iron	Fe	55·85	Tungsten	W	183·86
Krypton	Kr	83·80	Uranium	U	238·07
Lanthanum	La	138·92	Vanadium	V	50·95
Lead	Pb	207·21	Xenon	Xe	131·30
Lithium	Li	6·940	Ytterbium	Yb	173·04
Lutetium	Lu	174·99	Yttrium	Y	88·92
Magnesium	Mg	24·32	Zinc	Zn	65·38
Manganese	Mn	54·94	Zirconium	Zr	91·22
Mercury	Hg	200·61			

Note: The above atomic weights are based on O=16.   From 1960 the reference standard $^{12}C = 12$ will be adopted.   This change will *reduce* atomic weights by 43 parts per million.   The above figures should therefore be *divided* by 1·000043 to conform to the new scale; but for most purposes the changes are insignificant.

Michael O'Mahony
18 Richmond Terrace
Clifton
Bristol

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PRACTICAL PHYSICAL CHEMISTRY

PRACTICAL
PHYSICAL CHEMISTRY

By

ALEXANDER FINDLAY
Emeritus Professor of Chemistry, University of Aberdeen

REVISED AND EDITED BY

J. A. KITCHENER
Senior Lecturer in Physical Chemistry,
Imperial College of Science and Technology, London

Eighth Edition
With diagrams

LONGMANS

BIBLIOGRAPHICAL NOTE

AUTHOR'S PREFACE

By the end of World War II, when the need for a new edition of this work arose, I had already retired from teaching and was preoccupied with other activities. For a number of years practical physical chemistry had been rapidly developing in various directions, but I no longer had facilities for testing the suitability of the newer techniques for inclusion in a course for University students of Ordinary and Honours Degree standard. It became clear to me, therefore, that if this book were to continue to serve the needs of students of chemistry and physical chemistry, a thorough revision of it was necessary by someone actively engaged in the work of teaching and familiar with the developments which have taken place in the apparatus and methods of practical physical chemistry. Such a revision, I am glad to say, has been undertaken and, as I believe, successfully carried out by Dr. J. A. Kitchener, to whom I here express my thanks. As the work of revision has now passed out of my hands it is my fervent hope that this book, now greatly improved, may be found by future generations of students to be a reliable and helpful guide.

ALEX. FINDLAY

REVISER'S PREFACE

For nearly half a century Professor Findlay's "Practical Physical Chemistry" has been a familiar guide to University students of Chemistry, and its seven previous editions testify to the value of its presentation. Consequently, it is with a sense of privilege that I have undertaken the work of preparing the eighth edition, and my aim has been to bring the technical details up to date without changing the general character of the book. The standard of the work has been advanced a little, and, in keeping with modern trends in scientific writing, a more terse style has been adopted, particularly in sections which summarize theory or experimental methods.

The book has been completely re-set in Times New Roman type, and a new set of diagrams has been provided. Much new material has been introduced, while some of the older topics have been curtailed in order to give a distribution of subject matter more in accord with modern interests. It has been necessary to avoid too drastic a change in order to preserve continuity for Colleges which base their practical courses on this book. However, the development of the subject has already reached the stage where there are more techniques available than can be illustrated in the time usually assigned to practical physical chemistry; consequently, experiments which merely serve to illustrate a point of theory and employ only common analytical apparatus must tend to give place to those which offer the student both experience with an unfamiliar piece of physico-chemical apparatus and also a useful theoretical exercise.

The experiments have been designed to illustrate the common techniques of physical chemistry *in their usual, basic form* avoiding, on the one hand, crude improvised apparatus and, on the other hand, elaborate instruments or complicated combinations of operations. A cardinal principle of experimentation—often ignored—is that the best method is generally the simplest one.

Advanced research techniques such as those used in X-ray diffraction, infra-red spectrometry and radio-chemistry, are outside the scope of this book, but a few "key" references to specialized monographs have been included for the benefit of advanced students.

It is a pleasure to acknowledge my great indebtedness to many past and present colleagues at Imperial College, who have either originated experiments incorporated in this edition, or in other ways given me the benefit of their experience. In particular I should like

to thank Drs. F. C. Tompkins, D. J. G. Ives, C. F. Cullis, and G. J. Hills. I am also grateful to Professor Findlay for his Preface, for encouragement, and for assistance in reading the proofs; and to members of the staff of the Publishers for their admirable co-operation.

It is too much to hope that a re-set, detailed book of this kind will be free from errors. Corrections and suggestions for future editions will be gratefully welcomed.

J. A. KITCHENER

Imperial College of Science and Technology,
    London.

    August, 1953.

INTRODUCTORY NOTE ON ARRANGEMENT, BIBLIOGRAPHIES AND SYMBOLS

THE ARRANGEMENT OF THIS BOOK

Chapters 1, 2, and 3 deal with topics of general importance throughout practical physical chemistry, namely, the treatment of experimental data, the determination of weight, volume and length, and the measurement and control of temperature.

In the remaining 11 chapters, physical chemistry is treated systematically in its main, logical divisions, starting with the properties of pure substances in a single phase, and progressing through phase equilibria, etc., to the more complex systems such as those involving electrical energy, surface effects, etc.

Each chapter is sub-divided into self-contained *sections*, and these are labelled alphabetically, and indicated at the head of each page. In general, each section begins with a brief survey of the theory, and then describes the chief experimental methods employed in the field. Instructions for carrying out experiments are given in considerable detail, and the method of working out the results is indicated.

BIBLIOGRAPHIES

At the end of each section there is a short list of relevant standard works, monographs, and original papers (indicated in the text by superscript reference numbers), in that order.

The *standard works*, which are quoted by author only, are as follows:

Partington, *An Advanced Treatise of Physical Chemistry*, Vols. 1–5, 1949–54 (Longmans Green, London).

Weissberger (Editor), *Technique of Organic Chemistry*, Vol. 1, 2 parts, Physical Methods, 1949 (Interscience Publishers, New York) (3rd edn. in 4 pts. to be published 1960).

Reilly and Rae, *Physico-chemical Methods*, 4th edn., 3 vols., 1943 (Methuen, London) (5th edn. published 1954).

The Bibliographies have no claim, of course, to being comprehensive; their purpose is to provide the advanced student with a "key" to the vast store-house of original literature.

Appendix I consists of a brief bibliography of physico-chemical techniques which are not dealt with in the present book.

SYMBOLS AND ABBREVIATIONS

The symbols and abbreviations used in this book conform (with a few exceptions) to the recommendations of the Symbols Committee of the Royal Society, The Chemical Society, The Faraday Society, and The Physical Society in 1951. Copies of the Committee's report can be obtained from the Royal Society, Burlington House, London, W.1, price 9d. each.

In addition to recommending specific letters to represent physical quantities (e.g. U for internal energy, E for electromotive force, etc.), the report advised use of the following typographic conventions for the different kinds of symbol:

Physical variables, such as pressure, temperature, concentration, in *italic* (sloping) type; thus, *p, T, c*.

General constants, such as Avogadro's number, the gas constant, Planck's constant, in **bold italics**; thus, **N, R, h.**

Internationally accepted units, such as metre, gram, ohm, hydrogen-ion exponent, in roman (upright) letters without a stop; thus, m, g, Ω, pH. Units named after a person are given a capital; thus, V for volt.

Chemical elements in roman type; thus Li.

Mathematical operators in upright type, $\log_{10} p$, dy/dt, ΔU.

Abbreviations, other than units, in lower case letters with a full stop. A list of common abbreviations was given, and the following are a few examples frequently met in physical chemistry.

alternating current	. .	a.c.	melting point . . .	m.p.
atmospheric .	. .	atm.	molecular weight . .	mol. wt.
boiling point .	. .	b.p.	per cent	%
concentration .	. .	concn.	potential difference . .	p.d.
dilute . .	. .	dil.	relative humidity . .	r.h.
direct current .	. .	d.c.	solution	sol.
electromotive force .	. .	e.m.f.	specific gravity . . .	sp. gr.
freezing point .	. .	f.p.	ultra-violet . . .	u.v.
gram molecule .	. .	mole	vapour pressure . .	v.p.

CONTENTS

THE ACCURACY OF MEASUREMENTS AND TREATMENT OF RESULTS

1A. ACCURACY OF MEASUREMENTS

Introduction: the role of measurements

When the scientific method is brought to bear on a new problem, the first stage consists of *experiment*, the second *correlation* of observations, and the third the construction of a *theory* to explain the phenomena. Further experiments may then be needed to test the validity of the theory and extend the scope of the investigation. Innumerable examples could be found of the power of this approach in the various sciences.

Physics can claim to be the most advanced of the sciences, since it has reached the stage where the majority of its phenomena can be fitted into a scheme of *quantitative* theory. Consequently, experimental physical chemistry—that is, the investigation of the physical properties of chemical substances and the relation of these properties to chemical reactions—is concerned largely with *quantitative measurements*. *Qualitative* observations have their place in physical chemistry, but quantitative studies provide concrete data by which a hypothesis can be stringently tested.

It is true that a quantitative framework of theory is not always available for interpreting a new set of measurements. For example, at the present time the mechanical behaviour of suspensions (e.g. clay pastes) is being much studied (see Ch. 14) because of the great technical importance of such materials, but a fundamental, quantitative "treatment" of phenomena such as thixotropy (p. 346) has not yet been developed. Nevertheless, quantitative measurements are valuable in this field, although at present they must be classified as purely *empirical*—that is, the result of experiment without direct theoretical interpretation. The data provide a foundation upon which a theory can eventually be built.

It is therefore appropriate to begin a book on practical physical chemistry with a consideration of *measurements*, their trustworthiness, and the methods employed for using them to best advantage.

Attaining a suitable accuracy. No measurement is *exact*, excepting, perhaps, the counting of integral units such as the number of

1

α-particles entering a Geiger counter.   Measurements of mass, length, time, and all the derived properties such as volume, density, viscosity, etc., are inevitably of limited accuracy, and every such measurement is valid to a certain degree only.   It is not always realized that one should attach as much importance to ascertaining the degree of precision of a measurement as to recording the result.   Consider, for example, an imaginary investigation of the effect of, say, glycerol on the surface tension of water.   Suppose the surface tension of pure water had been measured once and found to be 73 dynes per cm, and then glycerol was added and a second measurement of surface tension gave 72 dynes per cm; would it be correct to conclude that glycerol lowers the surface tension of water?   The answer obviously depends on how precise the two measurements really were.   Perhaps they were quite rough, and a few repetitions would give 73, 74, 72, 72 for the first, and 72, 73, 72, 74 for the second. In this case the original difference between 73 and 72 is said to be "*not significant*".   It is clearly *essential* to be able to attach to the figures 73 and 72 some index of their reliability, because without such an index these measurements are quite worthless.   It is the principal object of this chapter to consider how uncertainties attaching to physical measurements arise and how they can be dealt with.

The precision of an experiment can always be improved by using better instruments, by taking more care in the measurements, and by giving attention to the method of determination employed.   The question is therefore implicit in the planning of every experiment —how accurately need the measurements be made?   The answer will depend entirely on the purpose of the experiment.   Thus, in the determination of important physical constants such as the velocity of light, Faraday's constant, and atomic weights, extreme care and attention to every detail are called for, but many of the measurements needed in physical chemistry can be made sufficiently accurately for the purpose in hand and with greater speed and convenience without pressing all the determinations to the limit.   For example, in finding the "order" of a chemical reaction (Ch. 13) it will rarely be necessary to determine the concentration of the reactants with the greatest accuracy possible to analytical chemistry.   Indeed, that would be a foolish waste of effort, if the object of the work were simply to decide whether the reaction was of first-order or second-order.

Clearly, the proper approach to an experiment is to decide first the *minimum* accuracy required for the purpose, and then to design the experiment to yield results of a slightly higher accuracy—to be on the safe side!   Throughout this book, however, it will be assumed that it is desired to achieve the best accuracy obtainable conveniently

with ordinary instruments such as are normally employed in physical chemistry laboratories. Naturally, for special researches it is possible to obtain or design instruments capable of attaining a still higher order of precision. For example, ordinary potentiometers (Ch. 12) serve to determine 1 volt to 0·1 millivolt, i.e. 1 in 10^4, but precision "vernier" potentiometers are obtainable with which an accuracy of 1 in 10^6 can be achieved.

Sources and types of "error". Having seen that a knowledge of the precision of measurement is as important as the measurement itself, it is next necessary to consider where the uncertainties arise.

Even simple quantities such as *length* have to be measured against some kind of scale which is itself subject to some uncertainty in manufacture. Further, the operation of comparing the object with the scale involves an element of judgment, and two observers may differ slightly in their decision as to the reading, particularly as it is generally necessary to *estimate* fractions of a division engraved on the scale. The final measurement of length is therefore seen to be subject to uncertainties due to the scale and to the using of the scale. These are typical examples of what may be called "instrument errors" and "random errors of observation". The technical term "error" should be understood to mean a "departure from the true value", not a mistake on the part of the observer.

If the quantity to be determined is more complex (e.g. molecular refractivity—see Ch. 8), a considerable number of measurements and operations may be involved before the final value is obtained. Errors in the individual measurements may or may not (in different cases) have an important effect on the final result (see below), but, in addition, another kind of error may be incurred, namely an "error of method". There is generally a theoretical relationship connecting the measured quantities with the final quantity; often, approximations have to be made *in the theory*, and it may happen, therefore, that the final result is of limited accuracy through no fault of the measurements. For example, consider the measurement of angular rotation of a suspended system by means of a galvanometer mirror with lamp and scale. The displacement of the spot of light on the scale is often considered to be proportional to the *angular deflection of the suspension*, but this is really only an approximation which assumes that $\tan \theta$ is proportional to θ. It is fairly accurate for very small angles, but less accurate as the angle increases; for example, $\tan 6° = 0·1051$, but $\tan 12° = 0·2126$, and therefore if the method were used (without correction) an error of about 1% would inevitably be incurred with deflections of this order, although the actual experimental quantity—the scale reading of the spot of light —might be measured much more accurately.

The above example of an error of method is a very simple one, and it would be easy in this case to refine the theory in order to eliminate the approximation altogether. In many cases, however, the theory behind an experiment may be already difficult, and certain assumptions and approximations may be unavoidable. The final result calculated by use of the theory is then subject to the errors inherent in the method, and it may be difficult to decide how much weight can be attached to the final result. With difficult research problems of this kind it is advisable to determine the required quantity, if possible, by two quite independent methods, as a check.

For the present purposes it will be sufficient simply to note the existence of *errors of method*, which can be detected only by careful scrutiny of the theory behind the measurements. The more practical problems presented by *instrument errors* and *random errors* can, however, be treated further.

Instrument errors. No instrument is perfect. However skilled the mechanic who makes it, there is a limit to its accuracy, and it is important for the observer using the instrument to ascertain where this limit lies. All reputable instrument makers provide *calibration data*, stating the reliability of the particular instrument as determined in a physical standards laboratory. After a period of use, however, or if no calibrations are available, it may be necessary to devise a method of checking and, if necessary, calibrating the instrument afresh.

The checking or calibration of an instrument usually requires the use of reliable *standards*—for example, standard weights, thermometers, resistances, voltaic cells (Ch. 12), etc.—which have themselves been checked and preferably supplied with a certificate from a standards laboratory such as the National Physical Laboratory at Teddington, Middlesex. In research work where high precision is important, *all* instruments should be carefully calibrated.

The calibration of weights and volumetric apparatus is described in Ch. 2. The calibration of instruments such as electrical resistances and potentiometers is best left to the makers, although a physical chemist should be prepared to make critical tests of such instruments.

Even if an instrument is considered to be very reliable, e.g. a refractometer by a reputable maker, it should still be checked at one or two points—for example, by determinations with substances of known physical constants. At this stage it will be realized that two distinct considerations are always involved in making a measurement, namely, the *reproducibility* of the reading, and the *absolute accuracy* of the value obtained.

If the operations of making a measurement are repeated a number

of times some idea is obtained of the *reproducibility* of the result. Probably slightly different results will be obtained each time (especially if a number of operations are involved), and the reproducibility of the reading will depend on the care and skill of the operator and on the imperfections of the instrument being used. On the other hand, the absolute accuracy might be considerably less than the reproducibility would lead one to expect, as, for example, if the instrument were out of adjustment. Measurements with pure substances can frequently help to decide how reliable an instrument really is.

This raises the question of instrument *corrections*, because unless all the necessary corrections are applied the full accuracy of the instrument is not obtained. Well-known examples of determinations where corrections must obviously be made are (a) weight, for buoyancy of the air (Ch. 2), (b) temperature, for emergent stem correction (Ch. 3), (c) barometric pressure, for expansion of the scale and gravitational field (Ch. 4), (d) thermocouple reading, for cold-junction temperature (Ch. 3). Wherever such corrections would make a significant change in the reading they should certainly be applied, and in physical chemistry any reported value is assumed to have been corrected.

There still remains the question of instrument defects, such as may be revealed by tests with substances of accurately known constants, even after all obvious corrections have been applied. The most common imperfections are (a) "zero" error due to displacement of a scale, (b) constant or proportional error arising from error in an electrical resistance, (c) "backlash" in an adjustable part of an instrument, due to poor mechanical construction or to wear, (d) eccentricity of a circular scale. In many cases it is possible to apply corrections to minimize errors from such sources; for example, the zero error may be determined, the effect of backlash can be largely eliminated by moving the adjustable part in the same direction every time, and eccentricity of circular scales can be overcome by taking readings on both sides of the scale (Ch. 8, p. 184).

With some instruments, however, a check at one point of the scale provides no guarantee that other parts of the scale are equally accurate. Thermometers and burettes are examples of instruments which obviously ought to be checked at a number of points.

Random errors of measurement. However good an instrument may be, there is a limit to the *reproducibility* of measurements. This may arise from slight difficulty in making the final adjustment (as in matching the fields in a polarimeter—Ch. 8), or in estimating fractions of a division on the scale (as on a thermometer), or from small irreproducible factors such as the sticking of a mercury

meniscus in a manometer.   In other cases the limit of reproducibility may be quite outside the instrumental measurements; it may be associated with the operations of preparing the material for measurement.   For example, the chief error in gravimetric analysis or determination of gas density (Ch. 4) is rarely the final weighing, but is generally bound up with the preparation and purity of the substance to be weighed, and the handling, drying, and temperature control of the crucible or bulb in which the substance is to be weighed.

When all obvious sources of error have been removed, it is still found that a number of complete repetitions of the work lead to slightly different values.   These "random errors" are usually only in the last place of figures which can be recorded, although sometimes, when the irreproducibility lies with the operations, the random error may be found to be much greater than the random errors of the instruments.

Random errors can be reduced by practical skill, care, and attention to detail.   A good example is the measurement of the optical rotation of a solution (Ch. 8); the determination involves a subjective judgment of the setting of the polarimeter to a position where the two parts of the optical field of view are of equal intensity.   The reproducibility will be found to increase as the observer becomes more practised, and it is also improved by darkening the room and arranging a comfortable position for the observer in order to reduce eye strain.   Such steps will reduce the random fluctuations on a measurement to a new, lower value, but it is still necessary to decide the magnitude of the uncertainties introduced by random errors, and to find some method of reporting and dealing with them.

Suppose a number of repetitions of a measurement are made by the same technique, with the same apparatus and care, and by the same observer (or observers).   The final results show small random differences, the values being sometimes slightly higher and sometimes lower.   How can the utmost information be extracted from the results?   Obviously the set of repeated measurements conveys more information than a single observation.   Firstly, the *arithmetic mean* of the results is almost certainly a more reliable value than a single observation; secondly, the observed deviations of the observations from the mean give an indication of the degree of reliability to be attached to a single observation (or to a mean of a number of observations).   For an adequate understanding of the proper treatment of random errors it is necessary to introduce some elementary theory of statistics (see below).

The problem can be most readily understood by considering an imaginary set of measurements of a length.   Suppose, for example,

the surface tension of a liquid is to be measured by the well-known capillary rise method. One quantity required is the radius of the tube, and the uniformity of the bore must also be examined. This is usually done by measuring the length of a weighed thread of mercury at different positions along the tube by means of a vernier travelling microscope. A good vernier microscope can be *read* to 0·001 cm, but doubtless if repeated measurements of the length of the thread of mercury were made there would be appreciable differences between them, arising from difficulties in setting the microscope, moving the mercury (with attendant "sticking" due to hysteresis of the contact angle, etc.). A set of consecutive readings might well give figures such as the following: 5·216, 5·213, 5·214, 5·218, 5·215, 5·213, 5·215, 5·211, 5·217, 5·216, 5·212, 5·213, 5·214, 5·214, 5·212.

The problem is to find a method of extracting a result of maximum accuracy from the data, together with an index of reliability.

Fig. 1.1(a) represents the sequence of results diagrammatically. It becomes evident as the repetitions proceed, that the "true" length probably lies somewhere between 5·215 and 5·213, and the figures obtained are merely random deviations on one side or other of the true result. This is seen clearly from

FIG. 1.1 Charts representing random deviations in the apparent length of a mercury thread, measured 16 times with a vernier microscope.
(a) The sequence of the readings obtained. (b) The mean of the readings, calculated after each additional reading.

Fig. 1.1(b), in which, at each stage, the mean of all the points so far obtained is plotted. It is evident that as the number of readings increases, the mean settles down gradually towards a constant value, which is slightly greater than 5·2140 but less than 5·2145. After sixteen readings there is little doubt that, to the nearest thousandth of a centimetre, the best result is 5·214, but the fourth decimal place is still in doubt.

The original readings were evidently deviating at random on either side of 5·214 by amounts up to 3 or 4 units on the last place. However, small deviations are more frequent than large, as can be seen

by plotting a *frequency histogram* which shows the number of observations falling in each interval of length (Fig. 1.2). The observations are evidently distributed more or less systematically about 5·214, positive and negative deviations of a given magnitude being approximately equally probable. A symmetrical histogram with a well-defined maximum is not obtained, however, unless a considerable number of observations are available; for example, the first six observations in the present series give a very peculiar histogram (see the numbering of observations in Fig. 1.2), and the "best" value could not be established to the third decimal place with any confidence.

On the other hand, if a very large number of observations were made, the frequency histogram would eventually become a practically smooth "*distribution curve*", the maximum of which would give the
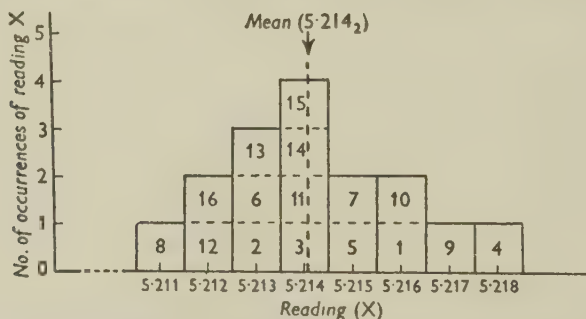
FIG. 1.2. Random deviations plotted as a frequency histogram
(data from Fig. 1.1).

"most probable value" with considerable precision. When only a small number of observations are available, it is useful to *assume* that they are a representative sample of an infinite number of observations, to which the well-established statistics of probability could be applied. If the deviations of the readings were entirely random (i.e. arose from a large number of small, independent positive or negative deflections), the frequency distribution would follow a theoretical law known as the "normal frequency distribution", or Gauss's "normal error curve" [1]. This branch of statistics is of great importance in some of the sciences into which physical chemistry sometimes trespasses, notably biology and agricultural chemistry. A brief account of the normal distribution curve is therefore given below. Some of its properties are used in the treatment of errors of observation in physical determinations.

The normal distribution (or "errors") curve. Consider some property (X) of a large number (n) of samples drawn from a given batch

of similar items which differ from one another only by small random deviations—for example, repetitions of a physical measurement, weights of individual ball-bearings from the same machine, size of wheat grains from the same sack, survival time of insect pests on a crop sprayed with insecticide, etc. The X values measured on individual samples will be X_1, X_2, X_3, etc., and will scatter about the arithmetic mean value, $\overline{X}$, which is defined by

$$\text{Arithmetic mean, } \overline{X} = \frac{X_1 + X_2 + X_3 + \ldots}{n} = \frac{1}{n}\Sigma X$$

It can be shown that if n is very large the frequency distribution curve (corresponding to the frequency histogram in Fig. 1.2) is given by the equation

$$y = \frac{1}{\sigma\sqrt{(2\pi)}} \exp\left[\frac{-(X-\overline{X})^2}{2\sigma^2}\right]$$

This distribution is shown graphically in Fig. 1.3 (curve A). In the equation, y has the meaning of a probability coefficient; any element of
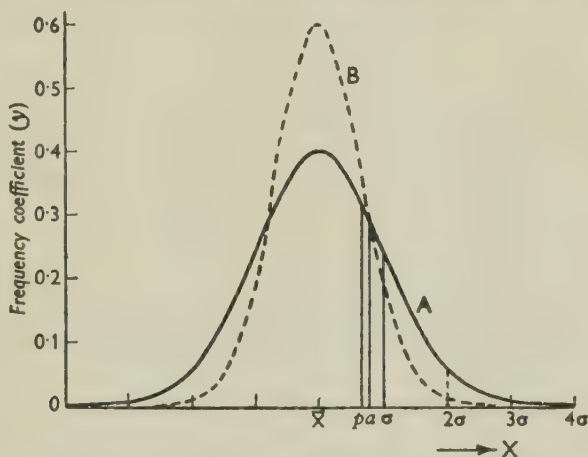
FIG. 1.3. Normal distribution ("error") curves.

area under the distribution curve corresponding to an increment from X to $(X+\mathrm{d}X)$, gives the *probability* that a single sample drawn from the batch will show an X value lying in the above range, X to $(X+\mathrm{d}X)$. The equation in the form given above has been arranged so that the total area under the curve (i.e. $\int_0^\infty y\,\mathrm{d}X$) is equal to unity, and therefore the area under the curve between X_1 and X_2 gives directly the fraction of the observations which lie between X_1 and X_2. Clearly, the most probable value to occur is that at the maximum of the curve (y a maximum), and this corresponds to the arithmetic mean of all the samples, namely $\overline{X}$. On the other hand,

a *single* observation is more likely to lie at some distance from $\overline{X}$, as, indeed, do almost all the observations.

The quantity σ in the normal frequency equation is a constant for a particular batch of samples, and it measures the *spread* of the curve—that is, the extent to which the X values deviate from $\overline{X}$. Curves A and B in Fig. 1.3 are typical normal distribution curves for two different batches which show the same mean value but different degrees of spread; on the average batch A shows greater deviations from $\overline{X}$ than does batch B. Such differing spreads of results might be obtained if a physical quantity were measured many times, first with a poorly made instrument and then with a very good one, or by a careless and a skilled observer using the same instrument.

The normal distribution curve is symmetrical about $\overline{X}$, since it is of the form $y = a \exp [b(X - \overline{X})^2]$, or

$$X = \overline{X} \pm \sqrt{(1/b) \log_e (y/a)}$$

The degree of spread of the data from $\overline{X}$ can be expressed in a number of ways. In statistics the quantity σ is most commonly used. This is called the *standard deviation* (σ), and is actually equal to the *root mean square deviation*, i.e. the standard deviation is defined (provided n is large), by

$$\sigma = \sqrt{(1/n) \Sigma (X - \overline{X})^2}$$

It can be shown [1], however, that if the number (n) of samples examined is small the estimate of σ obtained from them is, on the average, low by a factor of $\sqrt{(n-1)/n}$, and, consequently a better ("unbiased") estimate of σ is obtained by computing the standard deviation by the formula

$$\text{standard deviation, } \sigma = \sqrt{\frac{\Sigma(X - \overline{X})^2}{n-1}}$$

σ corresponds to the point of inflexion on the side of the probability curve.

Another possibility for measuring the spread is to use the *average or mean deviation*, (a), which is simply the mean difference between X and $\overline{X}$, without regard to sign, i.e.

$$\text{mean deviation, } a = \frac{1}{n} \Sigma |(X - \overline{X})|$$

Still another measure of the spread is the *probable error* (p); this is a deviation such that there is an equal probability of finding deviations larger than p and smaller than p. In Fig. 1.3 the ordinate through $(\overline{X} + p)$ bisects the *area* under the right-hand branch of the curve, and that through $(\overline{X} - p)$ does the same for the left-hand branch.

It can be shown that, for a normal distribution curve, these three ways of measuring the spread are slightly different in magnitude, but are related to one another by constant factors, namely $p = 0.6745\sigma$ and $a = 0.7979\sigma$ or approximately $p : a : \sigma = 3\frac{1}{2} : 4 : 5$. Their relative positions on the curve are shown in Fig. 1.3; 68.2% of the observations deviate by less than σ from the mean, and 95.5% are within 2σ. Only 1 in 400 should deviate by more than 3σ, and any such points are highly suspect and likely to be due to gross mistakes. Numerical values for the ordinates of the

normal probability curve and also the area under the curve (the cumulative percentage and derivatives) can be found in statistical tables.

Abnormal distribution curves (e.g. "skewed") will not be considered here.[2]

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1B. THE TREATMENT OF RESULTS

Statistical treatment of errors. It is clearly impracticable (and, indeed, unnecessary) to make a large number of repetitions of every physical measurement in order to study the distribution of the experimental errors. Instead, it may be assumed (in absence of evidence to the contrary) that if such laborious repetitions were carried out they would follow a normal errors curve. A few repetitions of one selected determination will therefore suffice to give an adequate indication of the reliability of the results.

Consider, for example, the first six readings of the set which has been discussed on p. 7. The arithmetic mean ($\bar{X}$) is 5·214(8); the average deviation (a) from the mean is $\pm 0·0015$, and the standard deviation (σ) is $\pm 0·0020$. The ratio a/σ for this set is fortuitously close to that expected for a complete normal distribution. The most probable error to expect (p) on a single measurement would therefore be about $0·67 \times \sigma = \pm 0·0013$. This information indicates the chance of getting near the correct value. If a *single* reading were taken, the probability is one half that it would not differ from the true value by more than $\pm 0·0013$. If the precision of the readings had already been known from previous work, the first result of the above series could have been reported as $5·216 \pm 0·001(3)$. The $\pm$ quantity written after a result is referred to as "the limits of error". This does *not* mean that the true value must inevitably lie between 5·214(7) and 5·217(3), but that there is a 50% chance that it does so. (In point of fact, the subsequent repetitions show that it probably lies just outside at about 5·214(2).)

Instead of quoting the "probable error", the "average deviation" or the "standard deviation" would have conveyed the same information. The probable error has been most used in physical sciences in the past, but it offers no real advantage over σ, which is more

directly derived from statistical theory. For purposes where the highest accuracy is required, it is probably best to report the "limits of error" specifically as the standard deviation, σ. For most purposes, however, the average deviation is quite good enough, and is more quickly calculated. In any case, unless a large number of repetitions are made, a will not differ significantly from p or σ. The result could therefore be reported as $5\cdot216\pm0\cdot001(5)$, meaning that determinations of this kind generally have an error of about $\pm0\cdot001(5)$.

If the final value is the mean of a number of repetitions, it is obviously more reliable than a single determination, and its limits of error are therefore smaller. It can be shown by statistical theory that if n equally reliable measurements are made, and the probable, average, and standard errors on a single measurement are known from previous measurements to be p, a, and σ respectively, then the corresponding *errors on the mean value* are $p/\sqrt{n}$, $a/\sqrt{n}$, and $\sigma/\sqrt{n}$. Thus, four repetitions would halve the uncertainty, but it would require 100 repetitions to get a mean with only one-tenth of the uncertainty associated with a single measurement.

Application of this relationship to the original sixteen readings leads to a final statement that the "best" value is $5\cdot2148$, and the standard deviation (s.d.) on this result is $\pm0\cdot0020/\sqrt{16} = \pm0\cdot0005$. (There seems little point in multiplying σ by $0\cdot67$ in order to report the "probable error".) The fourth place of decimals is now seen to be just significant, whereas on a single determination the third place of decimals was subject to uncertainty of one or two units.

Combination of errors. Most final results in physical chemistry are produced by calculations in which a number of measurements are combined. Thus, in arriving at the density of a gas (Ch. 4), the results of several weighings, and measurements of temperature and barometric pressure are employed. It is important to ascertain how the errors on the individual measurements affect the final result. This problem is sometimes called "the propagation of precision indices". Since the "errors" quoted after a result are statistical indices rather than definite limits, statistical theory is employed to find valid methods of combining the uncertainties. The following rules emerge [1]: they can be applied to any index of precision (e.g. σ, p, or a).

(a) *Sums or differences*

Suppose the quantities A and B are to be added (or subtracted) to give the quantity C, and the indices of precision (uncertainty) on A and B are a and b respectively, and the index of precision on C is c, such that $A(\pm a)+B(\pm b) = C(\pm c)$, then

$$c = \sqrt{a^2+b^2}$$

The error on a sum or difference is therefore greater than that on one of the quantities but less than the sum of the errors.

(b) *Products or quotients*

If
$$A(\pm a) \times B(\pm b) = C(\pm c)$$
or
$$A(\pm a)/B(\pm b) = C(\pm c)$$
then

$$c = C \sqrt{\left(\frac{a}{A}\right)^2 + \left(\frac{b}{B}\right)^2}$$

i.e. the *percentage* (or *fractional*) error on a product or quotient is equal to the square root of the sum of the squares of the percentage (or fractional) errors on the terms multiplied (or divided).

(c) *General case*

Functions more complicated than either (a) or (b) can be treated by the general rule:

If $U = f(X, Y \ldots)$ and the errors on $U, X, Y \ldots$ are $\pm \Delta U, \pm \Delta X, \pm \Delta Y \ldots$, then

$$(\Delta U)^2 = \left(\frac{\partial U}{\partial X}\right)^2 (\Delta X)^2 + \left(\frac{\partial U}{\partial Y}\right)^2 (\Delta Y)^2$$

In most cases it is found that there are one or two principal sources of error, and that all the other measurements incur negligible errors.

Examples

(1) If a vernier microscope can be read with an uncertainty of ± 0.002 cm, what is the uncertainty on the reading of a length?

Since the length is the difference of two microscope readings of equal accuracy, e.g.

$$L_1(\pm 0.002) - L_2(\pm 0.002)$$

then the uncertainty on the length is

$$\sqrt{0.002^2 + 0.002^2} \approx \pm 0.003$$

(2) What is the probable error in a determination of the density of mercury ($\rho \approx 13.6$) in a 25 ml pyknometer of weight 10 g, assuming that weighings, each reproducible to 1 part in 10,000, are the only significant sources of error?

Density is obtained by

$$\rho = \frac{\text{Wt. of mercury}}{\text{Wt. of water}}$$

$$= \frac{(\text{Wt. of pyknometer} + \text{mercury}) - (\text{Wt. of pyknometer})}{(\text{Wt. of pyknometer} + \text{water}) - (\text{Wt. of pyknometer})}$$

The weight of mercury will be about $25 \times 13 \cdot 6 = 340$ g, and the error in the numerator, by rule (a), will be about

$$\sqrt{\left(\frac{350}{10,000}\right)^2 + \left(\frac{10}{10,000}\right)^2} \approx \pm 0 \cdot 035$$

It is seen that the error arising from the weight of empty pyknometer is quite negligible compared with the error from the weight of (pyknometer + mercury).

Similarly, the uncertainty on the weight of water is

$$\sqrt{\left(\frac{25+10}{10,000}\right)^2 + \left(\frac{10}{10,000}\right)^2} \approx \pm 0 \cdot 004$$

If ρ is the density of mercury and the uncertainty is $\pm \Delta \rho$, then

$$\rho(\pm \Delta \rho) \approx \frac{340(\pm 0 \cdot 035)}{25(\pm 0 \cdot 004)}$$

By rule (b)

$$\frac{\Delta \rho}{\rho} = \sqrt{\left(\frac{0 \cdot 035}{340}\right)^2 + \left(\frac{0 \cdot 004}{25}\right)^2} = 1 \cdot 6 \times 10^{-4}$$

The error on the density is thus somewhat less than 2 parts in 10,000, in spite of the fact that *four* weighings, each uncertain to 1 part in 10,000, were involved.

(3) The molecular refractivity of a substance (Ch. 8) is defined by

$$[R] = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

where n = refractive index, M = molecular weight, d = density.   What is the percentage error on $[R]$ for benzene, if $n = 1 \cdot 498 \pm 0 \cdot 002$ and $d = 0 \cdot 879 \pm 0 \cdot 001$?   ($M = 78 \cdot 08$.)

The error on $[R]$ could be obtained by stages, using rules (a) and (b), but is best arrived at by the general rule (c).   This gives

$$(\Delta [R])^2 = \left(\frac{\partial [R]}{\partial n}\right)^2 (\Delta n)^2 + \left(\frac{\partial [R]}{\partial d}\right)^2 (\Delta d)^2$$

On substituting values, $[R]$ is found to be $26 \cdot 04$, and $\Delta [R] = \pm 0 \cdot 09$, and thus the percentage error is $\pm 0 \cdot 3\%$.

Number of figures to be employed.   Every measurement should be recorded to as many figures as are significant—no more, as that would implicitly claim a greater accuracy than justified, and no fewer, as that would incur loss of accuracy.   It is understood that the last figure quoted may be slightly in doubt, but it is probably correct to the nearest integer.   Thus a burette titration given as $25 \cdot 42$ ml is presumed to be valid to within $\pm 0 \cdot 005$ ml, and thus the end-point must have been sharp to within a fraction of a single drop of titrant.   The last figure is obtained by estimating tenths of a division on the scale.

Where the last figure is very doubtful, but dropping it might lose a little accuracy, it is useful to give it in parenthesis or as a subscript (e.g. $0.512(4)$ or 0.512_4); the implication here is that accuracy is better than ±0.001 but not as good as 0.0001.

When measured values are employed in a calculation, the same principles are followed—figures are retained to the limit of significance, but not beyond. For example, in adding 25·42 ml to 0·512 ml, the sum should be quoted as 25·93, *not* 25·932 ml, because the uncertainty is at least ±0.01 ml.

In multiplication or division it is only the *relative* or *proportional* error that matters, not the apparent or absolute value, and a given relative error in one of the numbers will produce a corresponding relative error in the result.

Suppose, for example, that one has to multiply two quantities given as 2·3416 and 2·55, and suppose each of these numbers to have the maximum apparent error; then the relative error in the first number is about 5 in 230,000, and the error in the second number is about 5 in 2,600. Evidently, therefore, the result of the multiplication will also have an error of about 5 in 2,600, or 0·2%. Consequently it would be incorrect to perform the multiplication in the ordinary manner, and write the result as 5·971080, for this result has a derived error of 0·2%, or of about 1 unit in the second place of decimals. All the figures after this are therefore meaningless, and should be discarded, the result being written 5·97.

When a number has to be *rounded off* to reduce it to a significant number of figures, the rule is that, for a 5 or over in the last figure rejected, the last retained figure is increased by one. Thus, 5·13462 if rounded to five figures becomes 5·1346, to four figures 5·135, to three figures 5·13.

Methods of calculation. If ordinary, long, laborious methods of arithmetic calculation are used they are liable to involve manipulation of a large number of useless figures which are afterwards discarded as meaningless. Time and mental energy can be saved by adopting abbreviated methods of multiplication and division, and by the use of logarithms and of the slide rule. These methods are also preferable because the chance of making an arithmetic error is reduced.

In making calculations with the aid of logarithms, the precautions adopted in the preceding methods for the avoidance of unnecessary figures are introduced automatically, if it be so arranged that the number of figures in the logarithm is greater by one than the number of figures in the least accurate of the numbers involved in the calculation. In this way one ensures that the error in the result shall not be greater than the error in the numbers from which the result is

obtained.   If one had to multiply $2·54 \times 4·3664 \times 0·89676$, one should use 4-place logarithm tables, and the second and third numbers should be rounded off to $4·366$ and $0·8968$.

The error inherent in the logarithm itself decreases with the number of places in the logarithm, each additional figure in the logarithm being accompanied by about a tenfold decrease in the error.   In the case of 4-place logarithms, the maximum possible error introduced into a calculation through their use may be taken as about 1 in 3,000. For work of moderate accuracy, 4-place logarithms will be sufficient; but in some cases, the error so introduced is greater than that due to experiment, e.g. in determinations of density.   In the latter cases, therefore, where the accuracy of the calculation is desired to be equal to the accuracy of the experiment, logarithms with 5 or 6, and even, in more exceptional cases, 7 places should be used.

In few, or none, of the experiments described in the following pages will an accuracy in calculation be called for greater than can be obtained by the use of 4-place, or, at most, 5-place logarithms. Frequently the accuracy required in practical physical chemistry will be considerably less.

For all calculations where the required accuracy of experiment or calculation is not greater than about 1 in 500, the slide rule is of great assistance.   It is also valuable for rapid, approximate checking of more accurate calculations.   With this instrument various degrees of accuracy can be obtained according to the size of the rule, but with the ordinary size of slide rule (25 cm in length) the accuracy obtainable may be put at about 1 in 500 to 1 in 800.   Considerably better accuracy can be obtained with special forms of slide rule such as Fowler's Calculator*; the "vest pocket" model resembles a watch of diameter $2\frac{3}{8}$ in, but it carries a series of concentric scales equivalent to a 30-in slide rule and can be read to about 1 in 1,000 to 1 in 5,000 at different parts of the scale.   A longer model is also obtainable.

Some types of modern physical research work (for example, X-ray crystallography) call for a great deal of accurate computation. Electric calculating machines are essential for such work, but where a moderate amount of accurate calculation is involved, hand-operated machines for multiplication or division can save much tedious labour.

Presentation of results.   Experimental work should be recorded at once in fullest possible detail, in a bound laboratory notebook. (Loose sheets are to be deprecated.)   It is to be expected that much that is recorded will never be used, because only final, successful measurements will be adopted.   The final result of the work will

* Fowler's (Calculators) Ltd., Hampson St. Works, Sale, Manchester.

usually be presented as a report or paper for publication. Such reports should contain all *essential* information about the work (according to the purpose of the report), but nothing superfluous. In modern scientific writing short, precise sentences are favoured, figures of speech are avoided, and an impersonal style of writing is generally adopted.

The most common lay-out for a scientific report is roughly as follows. Firstly, a brief introduction states the purpose of the work, and the principles on which the experimental work is based. Then follows a section giving all necessary details of how the practical work was carried out. Next comes a presentation of the experimental results together with evidence of their degree of reliability. Finally, a "discussion" section considers the final conclusions resulting from the whole work, and perhaps provides a theory to account for the observations. A common fault is omission of clear statements of the significance of the work. When data or evidence from other sources is quoted it is very desirable to find and refer to the *original* source of the information, rather than to employ data on trust at second hand.

The numerical results of practical work are most conveniently presented in the form of tables, supplemented, where necessary, by a summary of other data necessary to the calculations. It should be possible for a competent person reading the report to check any but elementary calculations. The general form of the results is most readily seen if they can be given also as a graph on which the experimental points are clearly plotted. The size of circles, triangles, squares or other symbols used to characterize the points should be approximately equal to the limits of error on the results. The abscissae should give the independent variable and the ordinates the dependent quantity. The scales should be so arranged that the data make full use of the paper, and they should be clearly graduated and the units stated.

Wherever possible, it is an advantage to employ in a graph such mathematical functions as will result in a straight line or a smooth curve of gentle curvature. For example, the vapour pressure of a liquid increases very steeply with temperature, but a graph of log (vapour pressure) is practically a straight line when plotted against $(1/T°K)$ (Ch. 5).

A straight line function is especially valuable for *interpolation* or *smoothing* of a set of results—a matter which deserves some consideration. A great many investigations in physical chemistry lead to a series of values of some function y for different values of an independent variable x. In most cases it is either known from theory or becomes apparent from the regular trend of the results that a

definite functional relationship exists between y and x, i.e. $y = f(x)$.*
The ideal treatment of the results is, then, to discover the nature of
the function and express the relationship as a mathematical equation.
The final equation then summarizes the result of the work in a more
convenient form than a table of experimental data, and it is probably
more reliable because it makes use of all the points.   Further, it
can be used for interpolation between the experimental values, and,
with less confidence, for extrapolation outside the experimental range.

The simplest method of fitting an equation to the data is to plot
a graph of suitable functions to produce a straight line relationship
and draw "the best" straight line by judgment, the aim being to
select a line to run as close as possible to the greatest possible number
of points.   The selection is necessarily somewhat arbitrary.   A
better procedure, which avoids personal judgment, is that known
as the "method of least squares" [3].

Fitting equations by the method of least squares.   This is a mathe-
matical method of finding the "best" values of the constants in a given
type of equation to fit the experimental data as well as possible.   The
criterion for the "best" fit is that the sum of the squares of the deviations
of the experimental points from the chosen line should be as small as
possible; this can be shown to correspond to the condition that the
arithmetic mean should be the "best" representation of a series of read-
ings of the same quantity.   It would hold if the deviations from the line
followed the normal errors distribution.   The method is applicable to
many forms of equation, but is chiefly used for straight lines—the only case
considered here.

Suppose the data consist of a set of n points, the co-ordinates of which
$(x_1 y_1, x_2 y_2, \ldots x_n y_n)$ are tabulated.   Suppose, further, the values of the
independent variable x can be regarded as subject to negligible error,
all the deviations being in the y values.   By hypothesis, these results are
scattered at random from the "true" line, the equation of which is taken
as $y = a + bx$.   The y deviations can then be written down.   Thus, for a
typical point, i, y_i should have been at $(a + bx_i)$, and the deviation is
therefore $y_i - (a + bx_i)$.   The sum of the squares of the deviations is
$\Sigma(y_i - a - bx_i)^2$ summed over all n points and this quantity must be made
a minimum by suitable choice for the values of a and b.   The condition for
a minimum is obtained algebraically by differentiating the expression with
respect to a and b, putting the derivatives equal to zero, and solving

* There is also, of course, another important type of investigation—rarely
encountered in physical chemistry, but very common in biology, agricultural
chemistry, operational research, etc.—in which it is desired to find whether any
correlation does exist between two properties; for example, whether the concen-
tration of certain trace elements in the soil affects crop yields, or whether there
is any connection between the silicon content and the sulphur content of pig-
iron produced by a blast furnace, etc.   This field of study requires special
statistical methods by which "coefficients of correlation" or significance tests
can be applied.   These methods are outside the scope of the present work; they
may be found in most textbooks of statistics.[2]

the resulting pair of simultaneous equations. *The final working formulae for obtaining the "best" constants are*

$$a = \frac{\Sigma x \Sigma xy - \Sigma y \Sigma x^2}{(\Sigma x)^2 - n\Sigma x^2} \text{ and } b = \frac{\Sigma x \Sigma y - n\Sigma xy}{(\Sigma x)^2 - n\Sigma x^2}$$

It is therefore necessary to draw up columns of the x and y values of the experimental points, and then tabulate x^2 and xy and add each column for insertion of the sums in the above formulae. The limits of error attaching to the constants a and b of the fitted equation ($y = a + bx$) can be calculated if the limits on a single observation are known; if, for a given value of x, the y value is ($y \pm \Delta y$) where Δy is the standard deviation, probable error or mean deviation, then the corresponding uncertainty on a is $\pm \Delta y / \sqrt{n}$ and on b is $\pm \Delta y / \sqrt{\Sigma(x - \bar{x})^2}$.

STATISTICAL EXPERIMENT

Investigate the reproducibility of a 5 ml pipette, and determine whether the addition of a wetting agent to the solution employed affects the volume which the pipette delivers and the reproducibility of the volume.

Procedure.   The method consists simply in weighing successive volumes of water delivered by the pipette.

Clean a 50 ml stoppered standard flask, a 5 ml pipette and a stoppered bottle of about 250 ml capacity. Take the temperature of the balance case. Fill the bottle with distilled water and adjust the temperature to that of the balance. Then proceed to weigh the flask with successive additions of 5 ml portions of water from the pipette until 10 portions have been added. The weighings should be made to the nearest milligram. A standard pipetting technique (drainage time, etc.) must be adopted.

Repeat the set of weighings using now water to which a small quantity of synthetic detergent has been added. Since the object of the detergent is to depress the surface tension, it is not necessary to add more than the minimum amount required to produce a stable foam when the solution is shaken. The change in density resulting from addition of the detergent will be negligible.

Treatment of results.   Calculate the weights (W) of water delivered by the pipette. Take the mean ($\bar{W}$) of the first 10 portions (A, without detergent) and of the second 10 (B, with detergent). Then work out the *deviations* from the mean, the *mean* deviations a, ($= (1/10)\Sigma|W - \bar{W}|$) and the standard deviations σ, ($\sigma^2 = (1/9)\Sigma(W - \bar{W})^2$ cf. p. 10). Compare the means and the standard deviations for the two sets of readings to ascertain whether the addition of detergent affects the volume delivered by the pipette and the reproducibility of the volume.

To decide whether $\bar{W}_A$ is *significantly* different from $\bar{W}_B$ may require a statistical test. One can calculate as follows the chance that the difference between $\bar{W}_B$ and $\bar{W}_A$, ($\bar{W}_B - \bar{W}_A$), might be obtained quite fortuitously on the mean of 10 random determinations *without series B being in any way different from series A.*

The function defined by

$$t = \frac{\text{(deviation of the mean of } n \text{ observations from the true mean)}}{\sigma/\sqrt{n}}$$

is known as "Students' t" (i.e. the ratio of the observed deviation to the standard deviation for n measurements). The probability of getting various values of t for given values of n is given in statistical tables.[4] Thus, if $n = 10$, the probability of getting $t > 1 \cdot 83$ is 1 in 10; similarly, the probability of finding $t > 2 \cdot 26$ is 1 in 20, $t > 2 \cdot 82$ is 1 in 50, $t > 3 \cdot 25$ is 1 in 100, and $t > 4 \cdot 78$ is 1 in 1,000. The value of t obtained experimentally with the 10 observations of Set B (taking $\overline{W}_A$ as the true mean) must therefore be considered in relation to these probabilities. For example, a value of t of about $3 \cdot 0$ would strongly suggest (though not prove) that set B is significantly different from set A, since the chance of getting a deviation of this magnitude in $\overline{W}_B$ by mere random deviations is small.

The *reproducibility* of the two sets of pipettings will be reflected in their respective standard deviations. It is most likely that σ_A and σ_B will differ somewhat, but again caution is needed before deciding that one set is more precise than the other, since the data are based on only 10 observations. The ratio F, defined by $F = \sigma_A^2/\sigma_B^2$ (or σ_B^2/σ_A^2, if $\sigma_B > \sigma_A$) is called the *variance ratio* (Fisher). From tables of F for the case $n_A = n_B = 10$ one finds that a 1-in-5 chance exists that 10 random observations might lead to a variance ratio of $> 1 \cdot 7$—that is, without any difference existing between set A and set B. Of course, the greater is F, the less chance is there that set B is merely a random lot like set A; thus, the chance of $F > 3 \cdot 0$ is 1 in 20, $> 4 \cdot 8$ 1 in 100, and $> 9 \cdot 0$ 1 in 1,000. If one finds, for example, $\sigma_A > 3\sigma_B$ ($F = 9$), this is strong indication that the B set of observations are significantly more reproducible than those of set A.

It will be noticed that the statistical treatment of the data does not lead to absolutely certain conclusions—only to conclusions of a definite degree of probability. If the degree of confidence (in a conclusion) indicated by a statistical test is not great enough to allow a satisfactory decision to be made, the data must be considered inconclusive, and the only thing to be done to get a more definite result is to make a much larger number of observations or more accurate ones.

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DETERMINATION OF WEIGHT, VOLUME AND LENGTH

Almost all experimental work in physical chemistry involves deter-
minations of *weight*, *volume* or *length*; furthermore, the majority of
more complicated properties such as density, surface tension, vapour
pressure, rate of reaction, etc., are translated in practice into these
fundamental measurements for convenience of study. Consequently,
a knowledge of the most appropriate methods of measuring weight,
volume and length in different circumstances is highly important; the
general methods are well known, but it is equally important to con-
sider the degree of accuracy that can be achieved with the various
instruments, and the technique and precautions which must be
adopted to obtain the highest possible accuracy. The calibration
of weights and of volumetric apparatus is essential for all but
approximate determinations (e.g. better than 1%). Methods of
calibrating other measuring instruments will be described as occasion
arises.

2A. DETERMINATION OF WEIGHT

The balance. The modern analytical balance is a highly refined
and indispensable instrument, and the determinations of weight can
be made very accurately without great difficulty; for example, an
object of about 100 g can readily be weighed correct to the nearest
milligram, i.e. 1 part in 10^5. No other quantity can be determined
with this accuracy in an ordinary laboratory. In fact, the accuracy
of the balance is generally greater than the accuracy with which a
body can be defined or reproduced. Thus, in weighing glass vessels
or other material used in an experiment, the difference in weight
due to *handling*, manner of drying, etc., often amounts to several
tenths of a milligram, while the balance itself might be capable of
weighing to 0·1 mg. A *significant* accuracy of 1 in 10^5 is not
achieved without (a) a balance of excellent workmanship and in
proper adjustment, (b) rigorous attention to the technique of weigh-
ing, handling, etc., and (c) a set of carefully calibrated weights.

The first requirement which a balance must satisfy is that it shall
be consistent with itself; i.e. successive determinations of the weight
of an object must be in agreement. From the closeness of agreement

between the different weighings, the accuracy of the balance can be judged. In the following paragraphs the proper use of an ordinary chemical balance will be considered. The modern "aperiodic" balance is described later (p. 28).

Determination of the zero point. Before using the balance, and also from time to time during a series of weighings, the zero point, or the position of rest of the beam when unloaded, should be determined. This is done by releasing the beam and allowing it to swing free. Readings are then taken of the extreme points on the scale reached by the pointer on either side of the middle line, two readings being made on one side of the middle line, and one on the other, the first swing being neglected. Suppose that the turning points on the right of the middle line were $+6\cdot0$ and $+5\cdot5$, while the turning point on the left side was $-5\cdot7$; then the turning point on the right corresponding with the point $-5\cdot7$ on the left is $\frac{1}{2}(6\cdot0+5\cdot5) = +5\cdot8$. The corresponding turning points are equidistant from the middle line, and the zero point is therefore correct.

On the other hand, suppose that the following turning points were observed, the readings on the right being called positive and those on the left negative: right $+6\cdot0$, left $-4\cdot5$, right $+5\cdot5$. Then the turning point on the right corresponding to that on the left is $\frac{1}{2}(6\cdot0+5\cdot5) = +5\cdot8$, and the resting point is therefore $\frac{1}{2}(5\cdot8-4\cdot5) = +0\cdot7$; i.e. the zero is $0\cdot7$ division to the *right*.

Rule. *To find the position of rest, take the mean of the two readings on the one side, and divide the algebraic sum of this mean and the reading on the opposite side of the middle line by 2; the result gives the scale division corresponding to the rest-point, and the sign ($+$ or $-$) indicates on which side of the middle line the rest-point lies.*

Two or three determinations of the zero point should be made, and the mean taken. With a good balance the different determinations should not differ by more than one or two tenths of a scale division.

Unless the zero point is considerably removed from the middle line, the adjustment of the balance need not be altered; but if it should be in excess of one scale division, the zero point should be corrected by means of the small screws at the ends of the beam, or of the metal flag which is above the centre of the beam.

Sensitivity of a balance; weighing by oscillations. In determining the weight of a body, weights to the nearest centigram are placed on the scale-pan of the balance, and the milligrams and fractions of a milligram then determined by means of the rider. The fractions of a milligram can, however, be determined more accurately by the method of oscillations. As this depends on the sensitivity of the balance, the latter must first be determined.

By the *sensitivity* of a balance is meant the displacement of the rest-point of the beam produced by an excess of 1 mg on either side of the balance. The sensitivity varies with the load on the balance, although, as a rule, not to any great extent, and should be determined, therefore, with different weights in the scale-pans. To obtain the sensitivity of a balance, place on one side of the balance a given weight, and counterpoise it to within 1 mg by means of weights and rider. Determine the rest-point by the method given above. Now alter the position of the rider by an amount corresponding to 1 or 2 mg, in such a direction that the rest-point is now on the other side of the zero point. The sensitivity is then given by dividing the number of scale divisions between the two rest-points by the difference of weight in milligrams.

Example. Suppose that with the weight of 10·354 g the rest-point is found to be $+1·2$; and with the weight of 10·355 g the rest-point is $-0·8$. Then the displacement of the rest-point by a difference of weight of 1 mg is 2·0 scale divisions; and the sensitivity is therefore 2·0 scale divisions for a load of 10 g.

The sensitivity can be increased or diminished by raising or lowering the centre of gravity of the swinging parts of the balance by means of the so-called gravity bob, with which the better balances are furnished. Increase of sensitivity, however, entails increase in the time of swing, and should not be carried too far.

Having determined the sensitivity of a balance at a number of different loads in the above manner, the operation of weighing can be shortened, because it is only necessary to adjust the weight to the nearest milligram, and to determine the rest-point, provided the zero point has been previously determined. The fractions of a milligram can then be calculated from the difference between the rest-point with a given weight and the zero point, and from the sensitivity of the balance.

Example. Suppose that the zero point of the balance is $+0·5$, the rest-point with the weight 10·354 g, $+1·2$, and the sensitivity 2·0 scale divisions. Then the additional weight required is $\frac{1}{2}(1·2-0·5) = 0·35$ mg. The correct weight is therefore 10·35435 g.

The weight has here been expressed to five places of decimals, but whether or not the last place has any meaning will depend on whether the weight of the object remains constant to within one or two hundredths of a milligram. If it may vary by some tenths of a milligram, it will evidently be absurd to state the weight to five places of decimals. To weigh correctly to one or two units in the fifth decimal place demands experience and great care, so that in ordinary work a greater accuracy than one or two units in the fourth place of decimals cannot be expected.

In all cases where only differences in weight are in question a slight inequality in the length of the arms of the beam will have no influence, provided the object to be weighed is always placed on the same side of the balance. This, of course, should be made a rule.

It should be unnecessary to emphasize here that accurate weighings can be expected only if the balance is kept clean and free from dust, and if the beam is released and arrested in such a manner as not to cause jarring of the knife-edges. The beam must never be released with a jerk, and should be arrested only when the pointer is passing the middle point of the scale. The balance, also, should not be exposed to unequal heating, and should not, therefore, be placed in a window exposed to direct sunlight. A balance in general use in a large laboratory should be regularly inspected, and, if necessary, cleaned and adjusted by a competent instrument mechanic.

Calibration of weights. Even after the adjustment and accuracy of the balance have been tested in the manner described above, the accuracy of the weighings will still depend on the accuracy of the weights employed. Before undertaking accurate weighings, therefore, it is necessary to determine the errors in the weights; and even in cases where great accuracy is not aimed at, a set of weights should always be calibrated, for errors of quite appreciable magnitude are sometimes found, even in expensive sets. Also, sets of weights are liable to deteriorate over a period of use in a chemical laboratory.

Short method, using standardized weights. If a complete set of standardized weights is available, it is a simple matter to calibrate another set against the standardized ones, weighing by the method of substitution to eliminate possible errors in the balance arising from inequality of the arms (see below). In this method the object to be weighed is first counterbalanced by means of a "tare", that is, any convenient adjustable mass, the weight of which need not be known —weights from a spare set are, of course, ideal. The object is then removed from its pan and is replaced by weights until the same rest-point is reached. The weights required are equal to the weight of the object, independent of the length of the arms of the balance.

To calibrate weights by the substitution method, therefore, a tare is placed on the right-hand scale-pan and the standard weight on the left, and the rest-point determined. If this differs greatly from the zero point of the scale, the rider should be used in order to bring the rest-point to within 1–1·5 scale divisions of the zero. (It is an advantage to work with the rider in the middle position of the balance arm; this can be arranged by keeping an extra 5 mg weight on the *left hand* scale-pan throughout the whole operation of calibration.) Having determined the rest-point with the standard weight, the latter is replaced by the weight to be standardized, and the rider

then moved, if necessary, so that the same rest-point is obtained as with the standard weight. (Here also the method of oscillations should be employed.) In this way, the relation between the standard weight and the weight to be standardized is at once obtained. In the same way the different weights may be compared with one another.

Kohlrausch's method. Given only a set of unstandardized weights, it is possible to calibrate them accurately with respect to one another, as described below. This calibration will, of course, be only in terms of relative, not absolute mass, and one of the weights (e.g. the 50 g) will have to be taken as an arbitrary "standard" for the set. However, many chemical operations, such as gravimetric analysis, require only relative weights. If absolute calibration is required, one reliable standard weight must be available.

The principle of Kohlrausch's method is comparison of each weight in the set in turn, with a suitable selection of the others. It is possible to counterbalance any weight in the set; thus, if the brass weights consist of 50, 20′, 20″, 10, 5, 2′, 2″, 1 (the ′ and ″ distinguishing the duplicates), the 50 can be compared with $(20'+20''+10)$, 20′ with 20″, 20″ with $(10+5+2' +2''+1)$, and so on right down to the 10 mg which can be compared with the rider on position 10 on the balance arm. Unless the weights are perfectly accurate, each check weighing will reveal small differences between nominally equal collections of weights. These differences (which may be denoted δ_1, δ_2, etc.) must be determined very accurately (by means of the rider and the method of oscillations, using the precautions mentioned below); some will be positive, others negative. The weighings will therefore lead to a set of simultaneous equations of the following kinds (in which (50) means *the piece marked* 50 g, etc.), e.g.:

$$(50) = (20') + (20'') + (10) + \delta_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$(20') = (20'') + \delta_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$(20'') = (10) + (5) + (2') + (2'') + (1) + \delta_3 \quad . \quad . \quad . \quad . \quad (3)$$
$$(10) = (5) + (2') + (2'') + (1) + \delta_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and so on through the brass and fractional weights down to

$$(0 \cdot 05) = (0 \cdot 02') + (0 \cdot 02'') + (0 \cdot 01) + \delta_{n-3} \quad . \quad . \quad . \quad . \quad (n-3)$$
$$(0 \cdot 02') = (0 \cdot 02'') + \delta_{n-2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (n-2)$$
$$(0 \cdot 02'') = (0 \cdot 01) + (\text{rider at 10 mark}) + \delta_{n-1} \quad . \quad . \quad (n-1)$$
$$(0 \cdot 01) = \text{Rider at 10 mark} + \delta_n \quad . \quad . \quad . \quad . \quad . \quad (n)$$

If there are $(n+1)$ weights (including the rider) there will be n equations. By taking any one weight as correct (i.e. as internal standard for the set), the weights of all the other n pieces can be obtained by solving the n simultaneous equations. The simplest method of calculation is to start by taking the 0·01 g piece as a temporary reference. From equations (n) and $(n-1)$ one obtains

$$(0 \cdot 02'') = 2 \times (0 \cdot 01) + \delta_{n-1} - \delta_n$$

Substituting in equation $(n-2)$

$$(0 \cdot 02') = 2 \times (0 \cdot 01) + \delta_{n-1} - \delta_n + \delta_{n-2}$$

Substituting in equation $(n-3)$

$$(0.05) = 5 \times (0.01) + 2\delta_{n-1} + \delta_{n-2} + \delta_{n-3} - 2\delta_n$$

And so on up to the 50 g piece. The numerical δ values (carrying their proper sign) are summed step by step, and the apparent values of all the pieces in terms of the (0.01) piece can be tabulated. The final step in the calculation is to correct all the values to bring them into conformity with the 50 g piece as standard instead of the 0.01 piece which, for convenience of computation, has been taken as temporary standard. Suppose, for example, that after the computation based on (0.01) as standard, the $(50$ g$)$ worked out to be $50.0125(6)$ g. Then all the figures obtained for the individual pieces must be multiplied by $50/50.0125(6)$.

It is clear that in calibrating weights, the small differences (δ values) between the nominally equal weights, or sets of weights, must be determined with the highest possible accuracy. The following precautions are necessary: (a) all weighings must be made by the method of oscillations, the sensitivity being determined at different loads, and the readings recorded to the fifth decimal place of a gram: (b) an extra 5 mg weight should be kept on the left-hand pan so that the rider is always used near the middle of the balance arm: (c) the possibility of inequality of the lengths of the balance arms must be taken into account by using either the method of weighing by substitution with tares (see above) or the method of double weighing. In the latter method the first weighing is made with the body on the left scale-pan and weights on the right. (Let the weight to balance be W_1.) The object is then transferred to the right pan and weighed again, with weights on the left side. (Wt. found W_2.) If L and R are the effective lengths of the left and right arms of the balance, it follows from the theory of levers that the true weight is $\sqrt{(W_1 W_2)}$; but if W_1 and W_2 differ very little, the geometrical mean is practically the same as the arithmetic mean $\frac{1}{2}(W_1 + W_2,)$ which is therefore employed. In other words, in the method of double weighing, inequality of balance arms can be allowed for by taking the mean of the weights on the left and the right side. If a number of weights must be determined time can be saved by calculating the ratio of the balance arms R/L from one double weighing by the relationship $R/L = W_2/W_1$. Future single weighings can then be corrected by use of this factor, since the true weight of an object which, when placed on the left pan, needs W' g on the right to balance it, must be $W' \times R/L$. With a good balance, of course, R/L differs very little from unity, but the difference may yet be significant; further, R/L changes slightly with the loading of the balance owing to inequality of the strains.

Correction for the buoyancy of the air. In accurate determinations of the weight of a body, the apparent weight, i.e. the sum of the face

values of the weights used (corrected as described above) must be corrected for the buoyancy of the air; for a body will appear lighter by an amount equal to the weight of the air displaced.   The greater the difference in the density or the specific volume of the body and the weights used to counterpoise it, the greater will be the correction.

If a body of the density d is counterpoised by brass weights of the value G g, the volume of the body will be G/d ml, and its weight will therefore be diminished by $0.0012G/d$ g, where 0.0012 g is the weight of 1 ml of air under ordinary conditions (mean room temperature, normal pressure, and average humidity).   The true weight of the body would therefore be $(G+0.0012G/d)$ g, if the true weight of the counterpoise were G g.   But the brass weights by which the body is counterpoised have a volume equal to $G/8.5$ ml, where 8.5 is the density of brass; and they therefore suffer a diminution in weight of $0.0012G/8.5$ g.   The true weight, G_0, of the body is therefore equal to $G+(0.0012G/d)-(0.0012G/8.5)$ or

$$G_0 = G(1+0.0012/d-0.0012/8.5) = G(1+0.0012/d-0.00014)$$

In order, therefore, to obtain the true weight (i.e. the weight which the body would have in a vacuum) of a body weighed in air with brass weights, one must *add to each gram apparent weight* (G) the quantity $(0.0012/d-0.00014)$ g.   The following table given by Kohlrausch gives the value of this correction in milligrams for different values of d.

TABLE 2.i

Buoyancy corrections for bodies of various density

d	Correction	d	Correction	d	Correction
0·7	+1·57	2·0	+0·457	9	−0·010
0·8	+1·36	2·5	+0·337	10	−0·023
0·9	+1·19	3·0	+0·257	11	−0·034
1·0	+1·06	3·5	+0·200	12	−0·043
1·1	+0·95	4·0	+0·157	13	−0·051
1·2	+0·86	4·5	+0·124	14	−0·057
1·3	+0·78	5·0	+0·097	15	−0·063
1·4	+0·71	5·5	+0·075	16	−0·068
1·5	+0·66	6·0	+0·057	17	−0·072
1·6	+0·61	6·5	+0·042	18	−0·076
1·7	+0·56	7·0	+0·029	19	−0·080
1·8	+0·52	7·5	+0·017	20	−0·083
1·9	+0·49	8·0	+0·007	21	−0·086

It should be pointed out that although the above correction factor is adequate for most work it is not quite accurate enough if a precision of 0·1 mg on 50 g (100 ml object) is required, since the density of the air varies with temperature, pressure and humidity.   Also, there is the question

whether the weights employed have been standardized for weight in air or weight in vacuum.

Because of the uncertainties associated with correction for buoyancy, it is usual when weighing large objects accurately, to employ a counter-poise of approximately the same size as the object. Vacuum corrections are then needed only for the small differences between the volumes of the objects on the two scale-pans. An example of this procedure is found in the determination of the density of a gas by the globe method (Ch. 4).

Other precautions in accurate weighing. Appreciable errors are incurred if objects are not allowed enough time to reach the same temperature as the balance. A platinum crucible needs at least 20 minutes in a desiccator after heating and then 10 minutes in the balance, and larger objects may need considerably longer. Clearly, a trial should be made to find the minimum that will suffice.

The surface condition of large pieces of glassware is not easily repro-ducible, but wiping with a clean chamois leather is usually recommended, and heating by the warmth of the hand must be minimized. Needless to say, chemicals should always be weighed in a closed vessel. The balance pans may be dusted with a camel-hair brush. Temperature differences in the balance which might be caused by sunlight or artificial light are to be avoided, and, for the same reason, the person weighing should use the side doors of the balance case rather than the front.

The air-damped, "aperiodic" balance. Most of the time-consum-ing tedium of weighing is eliminated by the air-damped balance with automatic fractional weights. Fig. 2.1 shows a modern balance with these features. The oscillations of the beam are heavily damped by the viscous resistance of air in the small gaps between the pairs of concentric cups, the outer ones being fixed and the others attached to the balance arms. After a few seconds the balance settles down into a position of equilibrium, and the steady deflection is read on a small screen. The usual pointer is replaced by a minute glass scale, and a magnified image of this scale is projected by an optical system on to the screen. The sensitivity of the balance is carefully adjusted to make the image of the scale read directly in milligrams and tenths of milligrams. In using this balance, the object is balanced to the nearest gram in the usual way, and then the balance case is closed and the tenths and hundredths of a gram are added in the form of rings of wire which can be lowered into position on a cross strut on the right-hand arm by rotating graduated dials on the outside of the balance case. After balancing to the nearest 0·01 g, the next two places of decimals are read off as soon as the image of the graduated scale has come to rest on the screen. This type of balance is advantageous where many accurate weighings have to be made, as in gravimetric analysis, and only economic considerations save the traditional balance from being rapidly superseded for every purpose.

Other methods for determination of weight. Various modifications of the ordinary balance are available for large or small masses; thus, an "assay" balance may be sensitive to 0·01 milligrams and take a load of 2 g, and a modern micro-chemical balance will weigh 20 g, with a sensitivity of 1 microgram per division.

Torsion wire balances are useful for repetitive work with similar objects (e.g. weighing electric light filaments); loads up to 1 g can be weighed with
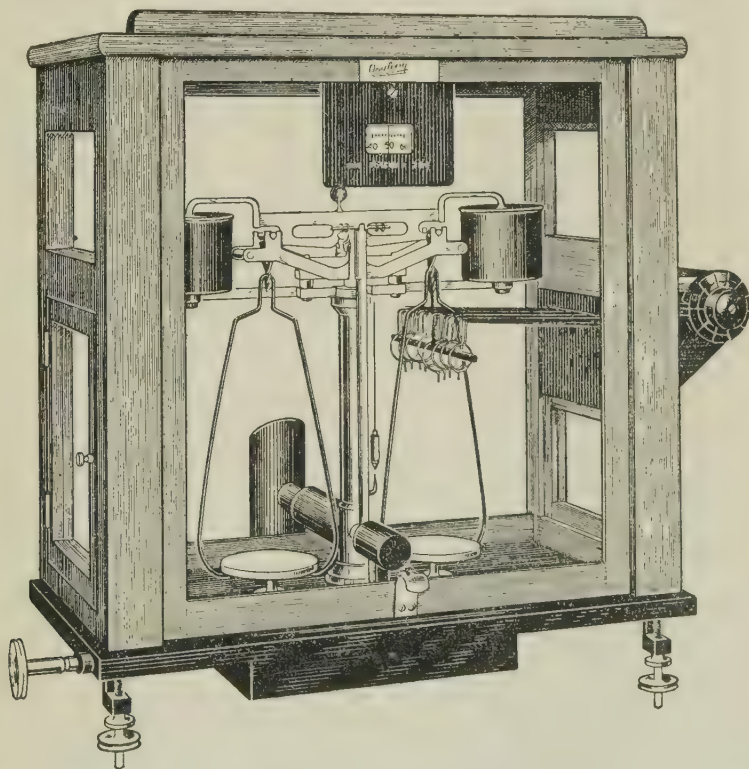

Fig. 2.1. A modern air-damped, "aperiodic" balance.
(Courtesy Messrs. Oertling, London.)

an accuracy of 0·2%. Torsion balances are found of use in measuring surface tension (Ch. 5).

In research work it is sometimes necessary to carry out a weighing inside a glass apparatus, e.g. for studying adsorption of gases by solids; the best known of the many methods which have been devised are the quartz spring balance of McBain and Bakr [1] (load 0·5 g, sensitivity 0·2 mg), the electro-magnetic balance (used, for example, by Gregg [2]) and the tungsten wire micro-balance of Gulbranson [3] (load 0·7 g, sensitivity 3×10^{-7} g). With modern forms of the quartz micro-balance [4] it is

possible to detect the increase of weight accompanying e.g., adsorption of a *monolayer* of gas on a piece of copper foil. Various automatically recording balances have been devised for following changes of weight.

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2B.   CALIBRATION OF VOLUMETRIC APPARATUS

By international agreement, the unit of volume is the *litre,* which is defined as the volume occupied by 1 kilogram of pure water at the temperature of maximum density and under normal atmospheric pressure, the weight being reduced to vacuum.   Although, originally, 1 kg was intended to be the mass of 1,000 cubic centimetres (cm^3) of water, actually the kilogram is now simply the mass of the "kilogramme des Archives" preserved in Paris; and since this mass is not exactly equal to the value as originally defined, the definition of a litre and of a cubic centimetre are no longer directly related in theory.   Experimentally, one finds, 1 litre = 1,000·028 cm^3, or 1 cm^3 = 0·00099973 litre.   The thousandth part of a litre, a *millilitre* (ml) is equal to 1·000028 cm^3.

Volumetric apparatus is nowadays calibrated in "ml", and although the older term "cc" is occasionally used, it can be taken as synonymous with "ml" for all ordinary purposes.

In order to determine a given volume, one determines the weight of a liquid, generally water (distilled), required to fill the volume, the weight being reduced to vacuum.   To save the trouble of making this reduction, use can be made of Table 2.2, which gives the volume (in ml), corresponding to an apparent weight of 1 g of water (i.e. weight in air), and the apparent weight of 1 ml of water, at different temperatures.   The table applies strictly only when the weighings are carried out with brass weights.

Calibration of measuring flasks. Volumetric glassware can be bought in two grades in Britain.   The permissible limits of error in "Grade A" and "Grade B" apparatus have been laid down in a scheme prepared by the Metrology Divison of the National Physical Laboratory.[1]   The percentage error decreases with increasing size of vessel.

Although the flasks made by the best makers will, as a rule, be found sufficiently accurate, no flask should be employed for accurate work without being tested.

TABLE 2.2

The apparent specific weight and apparent specific volume of water, weighed in air

Temperature °C	Apparent weight of 1 ml of water	Volume corresponding to an apparent weight of 1 g of water
10	0·9986	1·0013
11	0·9985	1·0014
12	0·9984	1·0015
13	0·9983	1·0017
14	0·9982	1·0018
15	0·9981	1·0019
16	0·9979	1·0021
17	0·9977	1·0023
18	0·9976	1·0024
19	0·9974	1·0026
20	0·9972	1·0028
21	0·9970	1·0030
22	0·9967	1·0033
23	0·9965	1·0035
24	0·9963	1·0037
25	0·9960	1·0040

To calibrate a flask, it is first cleaned and thoroughly dried; it is then counterpoised on a balance, and distilled water, having a temperature of 15° to 18°, is run into the flask until the lower edge of the meniscus stands at the level of the volume mark on the neck. Any water which may have got on the neck above the mark should be removed by means of filter paper. The weight of the water is then determined. (For flasks having a volume of 100 ml upwards, the weighings should be carried out on a robust balance which need not be accurate to less than a centigram: in the case of smaller flasks the weighings must be done on a more sensitive balance.)

The weight of the water contained in the flask up to the mark having been determined, the volume can be obtained from the table given above. For example, since an apparent weight of 1,000 g corresponds to a volume at 17° of 1,002·3 ml, the true volume of the flask is obtained from the expression $\dfrac{1,002·3 \times w}{1,000}$, where w is equal to the weights employed. If the error is at all considerable, a new ring should be etched on the neck in the correct position.

Etching glassware. It may also be necessary sometimes to graduate a flask for one's self. In this case the flask, after being cleaned and dried, is counterpoised on a suitable balance; the necessary weights are placed on the scale-pan, and distilled water is then poured into the flask until

equipoise is obtained.   In this case the last few millilitres should be intro-
duced by means of a pipette, any drops of water which may have formed
on the upper part of the neck being first removed by filter paper.   Since
from the table one finds that the apparent weight of 1 ml of water at 17°
is 0·9977 g, the weights necessary for any given volume can be calculated.

After the necessary amount of water has been introduced into the flask,
the latter is placed on a level table, and a strip of gummed paper is then
fixed round the neck, so that its upper edge coincides with the lower edge
of the water meniscus.   The water is then emptied from the flask, and the
neck coated with a thin, uniform layer of paraffin wax, extending some
distance on either side of the gummed paper.   When the wax has become
cold, a ring is cut by means of a knife along the upper edge of the gummed
paper.   The exposed glass is then etched by means of hydrofluoric acid,
the acid being rubbed into the cut in the wax by a little mop of cotton-wool
wound round the end of a stout copper wire.

Calibration of pipettes.   Pipettes are calibrated by weighing the
water which they deliver.   In carrying out the
calibration, however, several precautions must
be observed if an accuracy of 0·05% is to be
obtained.   In the first place, it must be seen
that the glass of the pipette is free from all
greasiness, so that the water runs from the
pipette without leaving drops behind.   If neces-
sary, therefore, the pipette must be thoroughly
cleaned.   This is best effected by filling the
pipette several times with a warm solution of
potassium dichromate strongly acidified with
concentrated sulphuric acid; or the pipette may
be left for some time full of the acid dichromate
mixture.   If the liquid is sucked up by mouth,
care must be taken not to suck the solution into the mouth.   As
this sometimes happens, owing to the end of the pipette being
inadvertently raised above the level of the solution, it is wise to
attach to the end of the pipette a safety tube of the form shown in
Fig. 2.2.

FIG.   2.2.   Safety
tube for use when
pipetting danger-
ous liquids.

Again, attention must be paid to the way in which the pipette is
allowed to deliver, and also to the time of delivery.   The pipette
should be held upright or, in any case, not sloping at an angle
greater than 45°, and the liquid allowed to run out freely.   Immedi-
ately the liquid stops running, touch the point of the pipette momen-
tarily against the side of the vessel, so as to remove the drop of liquid
which collects at the point, and then withdraw the pipette.   The
pipette, also, must not be allowed to deliver too rapidly, otherwise
varying amounts of liquid will be left adhering to the sides, and,
consequently, the volume delivered will vary.   The time of outflow

must therefore be regulated so that the time required for the delivery of a pipette of 10 ml capacity, or over, is from 40 to 50 seconds.   This can be effected by partially closing the end of the pipette in the Bunsen flame.

Having cleaned the pipette and regulated the time of outflow, the position of the mark on the stem is first determined approximately. To do this, a mark is made on the stem with a pencil for writing on glass, or with ink; distilled water is drawn up to this mark, and then allowed to flow into a previously weighed flask fitted with a stopper, and the weight of water determined. According as this weight is greater or less than the desired amount, a strip of gummed paper, with sharp cut edge, is placed round the stem of the pipette below or above the first mark; water is sucked up into the pipette, its level adjusted to the sharp edge of the paper strip, and the weight of water delivered determined. If the correct position has not yet been obtained, another strip of paper is fixed round the stem, and another weighing of the water delivered is made. Some idea of where this second strip must be placed will be obtained from the distance of the two marks apart. The second strip should be fixed at such a point that the weight of water is on the opposite side of the correct weight from that given by the first strip; i.e. if the former weight was too small, the second strip should be placed so as to give too great a weight. Having in this way determined two points on the stem of the pipette, such that the weight of water delivered is too great in the one case and too small in the other, the correct position of the mark can be calculated fairly accurately from the difference of the two weighings and the distance of the paper strips apart. A third paper strip should then be placed at the calculated point, and the correctness of the position tested by weighing the water delivered. Three concordant weights, the mean of which does not differ from the correct weight by more than 0·05%, must be obtained. To obtain the correct weight, use is again made of the table on p. 31, in order to find the apparent weight corresponding to the volume desired. The temperature of the water used should be that of the mean room temperature, 15°.

If a liquid other than water or aqueous solutions is to be pipetted accurately, the pipette must be calibrated specially with the liquid, as surface tension and drainage may differ.

For certain purposes pipettes are required to *take up* a definite volume of liquid; the modifications called for in the calibration procedure are fairly obvious.

The position of the mark on the stem having been determined, a ring is etched as explained.

Calibration of burettes.   Burettes are most simply calibrated by

the Ostwald method with the help of a small pipette (generally 2 ml), the volume of which has been accurately determined. The calibration pipette is attached to the burette in the manner shown in Fig. 2.3. The pipette may be kept in position by means of a loop of copper wire passing round the burette and the upper end of the stem of the pipette.

Before use, the burette and the pipette must first be thoroughly cleaned with dichromate and sulphuric acid. The pipette is then attached to the burett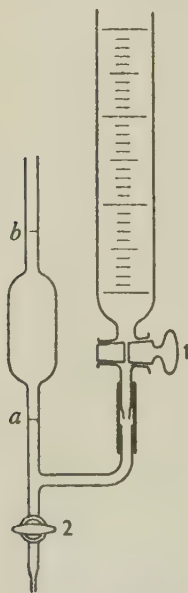e, and the latter filled full with water. The stop-cock of the burette is then opened so as to fill the side tube of the pipette and the lower part of the latter below the mark *a*, care being taken that all air-bubbles are driven out of the tubes. The level of the water is then adjusted so that it stands at the zero mark on the burette, and at the mark *a* on the calibration pipette. Tap 1 is then carefully opened, and water allowed to flow from the burette until it reaches the mark *b* on the pipette. A definite volume (say 2 ml), is thus withdrawn from the burette, and the reading on the burette is compared with this. Tap 2 is then opened, and water allowed to run from the pipette until it reaches the mark *a*, and is collected in a small flask which has been previously weighed. The flask should be kept corked except while water is being run into it. A further 2 ml of water is allowed to run from the burette, and a reading again made; tap 2 is again opened, and water allowed to run from the pipette until the level falls to *a*, the water being again collected in the weighed flask. These operations are repeated until the water has been run down to the lowest mark on the burette. The total weight of water thus run off is determined, and from this the volume of the calibration pipette is obtained. Knowing the volume of the pipette, and the corresponding readings on the burette, the corrections for the latter are obtained. Thus, suppose that the volume of the pipette was found correct, equal to 2 ml, and that the readings on the burette, after successive withdrawals of 2 ml, were 1·99, 3·96, 5·98, 8·02, 10·02, 11·98, etc., then the corrections to be applied at the points 2, 4, 6, 8, 10, 12, etc., ml on the burette would be +0·01, +0·04, +0·02, −0·02, −0·02, +0·02, etc., and at any intermediate point, the correction may be taken as proportional to

Fig. 2.3. Calibration of a burette by means of an auxiliary pipette.

the corrections on either side of it.   These corrections for every 2 ml may be written in tabular form; but it is better, especially if the corrections are considerable, to draw a curve of corrections, the burette readings being represented as abscissae, and the value of the corrections being represented as ordinates above (for positive corrections) or below (for negative corrections) the abscissa axis.   The correction values are then joined by straight lines, so that for any given reading on the burette the correction can be seen at a glance. Such a curve of corrections, plotted from the figures just given, is shown in the diagram (Fig. 2.4).

As with pipettes, so also in the case of burettes, attention must be paid to the rate at which the liquid is allowed to flow out.   The minimum time of outflow advisable will depend on the volume of liquid delivered; for 30 ml it should not be less than 40 seconds.

With burettes the accuracy to be attained is not in general as great as with pipettes. With a 30 ml burette of internal diameter of 8–10 mm an accuracy of about 0·1 per cent can be obtained on a reading of 10 ml.

The delivery of accurately measured fractions of 1 ml of liquid can be performed

FIG. 2.4. Correction chart for a burette.

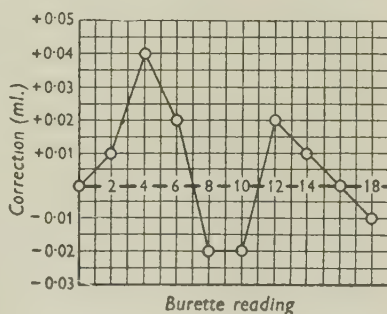by means of a micrometer syringe (p. 100).   Several other micropipettes and -burettes have been described.[2]

Parallax.   In making a reading of volume by means of a burette, etc., it will be found that as the line of vision is raised or lowered, the apparent position of the liquid meniscus alters.   Owing to this apparent change of position, to which the term *parallax* is applied, such volume readings are liable to considerable errors.   These can be avoided most easily by placing a piece of mirror glass behind the burette, and then raising or lowering the line of vision until the meniscus and its image just coincide.   The eye is then on the same level as the meniscus, and the error due to parallax disappears.   The reading is then made with the eye in this position. Burettes can also be obtained on which the main divisions are engraved completely round the burette.   With such burettes errors of parallax are readily avoided.

It will be clear that the precautions to be taken in reading a burette should also be taken when using apparatus of a similar character, e.g. the barometer, eudiometer, mercury manometer, etc.

BIBLIOGRAPHY 2B: Calibration of volumetric apparatus
Reilly and Rae, Vol. 1, Ch. 2 (4).
[1] National Physical Laboratory, *Volumetric Glassware* (*design, etc.*), 1954 (H.M Stationery Office, London).
[2] Conway, *Microdiffusion Analysis and Volumetric Error*, 1947 (Crosby Lockwood and Son, London).

2C. MEASUREMENT OF LENGTH

In addition to ordinary scales of boxwood, metal or glass (as used on mercury manometers, barometers, etc.), one frequently needs in physical chemistry instruments for measuring small lengths accurately.   The following principal types cover most requirements.

Vernier calipers similar to those used in engineering workshops will measure solid objects up to about 10 cm long, with an accuracy of 0·02 mm.   *Micrometer calipers* will read to 0·01 mm.   Both instruments can be obtained in a range of sizes.

The vernier measuring microscope is an extremely useful instrument. The common pattern with a traverse of about 25 cm will measure objects horizontally or vertically, and can be read to 0·02 mm.   The best instruments are readable to 0·01 mm.   The usual working distance for a travelling microscope is about 2 in.   A similar instrument furnished with a telescope instead of a microscope is called a *cathetometer*.   In measuring vertical distances with it, as on a manometer, care should be taken to set the scale vertical with a plumb-line, and to set the telescope horizontal by means of the spirit-level which is attached to it.

Small objects are measured on the stage of a microscope.   Most mechanical stages are fitted with a movement of about 50 mm and a vernier reading to 0·1 mm.   Micrometer eye-pieces can also be obtained; these contain a cross-wire which can be moved by a micrometer screw and the position can be read to 0·01 mm.

However, the simplest method of measuring microscopic objects is by means of an eye-piece scale which is slipped into the ocular of the microscope.   The effective magnification is obtained by comparing the graduations seen in the eye-piece with the fine lines engraved, or photographically recorded, on a glass graticule ("stage micrometer") which is examined through the microscope, using the same objective and ocular as used when measuring the object.

BIBLIOGRAPHY 2C: Measurement of length
Reilly and Rae, Vol. 1, Ch. 2 (1).

THE MEASUREMENT AND CONTROL OF TEMPERATURE

3A. TEMPERATURE MEASUREMENT

The fundamental scale of temperature. There are innumerable ways in which changes of temperature have been or could be measured; any physical property which is dependent on temperature and which is readily reproducible could be considered a potential basis for a "thermometer". However, no two substances or properties have *exactly* the same temperature-dependence, and consequently no two methods of thermometry lead to exactly the same scale of temperature. Temperature scales would therefore be entirely empirical and arbitrary if it were not for the existence of the absolute thermodynamic scale of temperature, devised by Kelvin (1851). The Kelvin scale is independent of the properties of any particular substance, being defined in terms of the efficiency of a hypothetical, thermodynamically reversible heat engine. Only the size of the degree is arbitrarily chosen by making the difference between the ice point and the steam point exactly $100°$.

Practical methods of thermometry have to be related to the absolute scale to eliminate their arbitrariness. The link between the absolute and the practical scales is the gas thermometer. It can readily be proved that if a gas obeyed the ideal gas laws precisely, its volume at constant pressure (or pressure at constant volume) would be exactly proportional to its absolute temperature. Consequently, in principle it is only necessary to compare a practical thermometer—say the mercury-in-glass—with a gas thermometer to determine the magnitude of any corrections which must be applied to the former to make it conform to the absolute scale. Unfortunately, the gas thermometer itself is not convenient to use, and further, no actual gas obeys the ideal gas laws accurately. Many supplementary data are required to correct the readings of a real gas thermometer to the ideal gas or absolute temperature scale. Consequently, the work of calibrating more practicable thermometers (notably the platinum resistance thermometer) on the absolute scale has been undertaken by national laboratories for physical standards and, as a result of such work, there was set up in 1927 a list of

six agreed "basic" fixed points covering the range $-183°$ C to $+1,063°$ C known as the International Temperature Scale. In addition, a number of "secondary" points have been determined and recommended for calibrating instruments other than the platinum resistance thermometer. These fixed temperatures are shown in Table 3.1, but reference must be made to the International report[1, 2] for the experimental procedures which must be followed to reproduce the various temperatures accurately. It is of

TABLE 3.1

The Fixed Points of the International Temperature Scale
(1948 Revision) *

	°C (Int.)
Fundamental Fixed Points	
Ice Point	0
Steam Point	100
Primary Fixed Points	
B.p. liquid oxygen	$-182\cdot970$
B.p. sulphur	$444\cdot600$
F.p. silver	$960\cdot8$
F.p. gold	$1063\cdot0$
Secondary Fixed Points	
Sublimation temp. CO_2	$-78\cdot5$
F.p. mercury	$-38\cdot87$
Triple point water	$+0\cdot0100$
Transition temp. $Na_2SO_4.10H_2O$	$32\cdot38$
Triple point benzoic acid	$122\cdot36$
B.p. naphthalene	$218\cdot0$
F.p. tin	$231\cdot9$
B.p. benzophenone	$305\cdot9$
F.p. cadmium	$320\cdot9$
F.p. lead	$327\cdot3$
B.p. mercury	$356\cdot58$
F.p. zinc	$419\cdot5$
F.p. antiminy	$630\cdot5$
F.p. aluminium	$660\cdot1$
F.p. copper	$1,083\cdot$
F.p. nickel	$1,453\cdot$
F.p. cobalt	$1,492\cdot$
F.p. palladium	$1,552\cdot$
F.p. platinum	$1,769\cdot$
F.p. rhodium	$1,960\cdot$
F.p. iridium	$2,443\cdot$
M.p. tungsten	$3,380\cdot$

* Stimson, *J. Res. Nat. Bur. Standards*, 1949, **42**, 209 (Research Paper 1962).

interest to note that above $1,063°$ C (the "gold point") the gas thermometer becomes impracticable, and the optical pyrometer is taken as standard, assuming the validity of Wien's law of radiation.

Method of measuring temperature. Fortunately in physical chemistry the problems discussed above can be taken as satisfactorily solved; there are enough well-established fixed points on the International Temperature Scale to facilitate calibration of any practical thermometer with adequate accuracy. The problem in practical physical chemistry therefore reduces to the choice of the most convenient method of thermometry for the temperature range involved. Table 3.2 (p. 40) summarizes some of the principal advantages and disadvantages of the chief methods of thermometry, and shows their useful range.

The platinum resistance thermometer is the most sensitive instrument available for measuring temperatures, but it is employed only in research work where the highest possible accuracy is needed. Similarly, accurate temperature measurement above 1,000° C is another specialized technique. Reference should be made to monographs on temperature measurement for further details of these methods.[3]

In ordinary laboratory work temperatures in the range 0–1,000° C are almost always measured with either a mercury thermometer or a thermocouple. Both need calibration. Mercury thermometers can be calibrated conveniently by comparison in a well-stirred water-bath with a standard thermometer for which a certificate (e.g. from the National Physical Laboratory) is available. Similarly, a base-metal thermocouple can be calibrated against a reliable platinum thermocouple.[4] The more general method, however, is to set up two or more suitable constant temperature baths of accurately known temperature, such as those in Table 3.1; the readings of the thermometer in these baths are determined and a calibration chart is constructed.

Mercury-in-glass thermometers are very convenient provided absolute accuracy of about 0·1° is sufficient. Higher accuracy can be obtained only with elaborate precautions to allow for the hysteresis of expansion or contraction of the glass, irregularity of bore, sticking of the meniscus when it is receding, and the influence of external pressure.[3] Normally a calibration at the steam point (using a hypsometer) and the ice point (obtained with pure melting ice in a thermos flask in which the thermometer is *suspended*) will show whether a thermometer is sufficiently reliable, and a third check at the transition temperature of sodium sulphate decahydrate (or transition temperature of some other salt in Table A.2, p. 352) can be added if temperatures some way from the fundamental interval are to be measured. (See Ch. 7, p. 138 for procedure). Incidentally, the transition temperature of sodium sulphate should read 32·48° on a perfectly accurate mercury thermometer rather than

TABLE 3.2

Method of thermometry	Useful range (°C)	Advantages	Disadvantages
Platinum resistance thermometer	−260° to +1,100°	Very high accuracy can be achieved. Suitable for close temp. control	Construction difficult: auxiliary apparatus costly: size large
Liquid expansion thermometers			
(a) Mercury in glass (ordinary)	−30° to +350°	Simple to use	Either range or accuracy limited
(b) Mercury in glass (hard glass, gas-filled)	−30° to +600°	Simple to use	Accuracy poor at high temperatures
(c) Alcohol in glass	−110° to +50°	Simple to use	Accuracy low
(d) Pentane in glass	−190° to +20°	Convenient for low temperature baths	Accuracy low
(e) Mercury in steel	−30° to +500°	Robust: Bourdon gauge indicator suitable for industrial use	Compensation needed for long emergent stem
Thermocouples			
(a) Copper-constantan	−250° to +400°	High thermo-electric e.m.f. (10–40 $\mu V/°$)	Deteriorates rapidly above 300°C: calibration needed
(b) Chromel-alumel	−250° to +1,100°	Usable for short periods up to 1,300°C	Frequent calibration needed
(c) Platinum/13% rhodium-platinum	−100° to +1,500°	Stable and reproducible: usable for short periods up to 1,700°C	High cost; low thermo-electric e.m.f. (4–12 $\mu V/°$)
Vapour pressure thermometers	Below room temp.	Sensitive and simple	Short range (c. 20°) covered by each thermometric liquid
Radiation pyrometers			
(a) Disappearing filament optical pyrometer	+800° to >2,000°	Covers range beyond Pt thermo-couple with accuracy ±5°	Calibration difficult: emissivity correction often needed
(b) Total-radiation pyrometer	+800° to >2,000°	Robust, direct reading, suitable for recording	As for (a): less accurate

the International value of 32·38 (Table 3.1). This is because the mercury-in-glass scale departs slightly from the absolute scale *between* 0° and 100° C, even although they are identical *at* these points; the departures in between depend on the thermometer glass, and reach a maximum of about 0·1° at 40° C.

Special mercury thermometers with high sensitivity (large bulb, narrow capillary, and short range) are used for measuring small changes of temperatures as in calorimetry (Ch. 9) and for determinations of the freezing points or boiling points of dilute solutions. The Beckmann thermometer is described in Ch. 6.

Emergent stem corrections. Thermometers are generally calibrated with the whole of the mercury thread immersed in a constant temperature bath, but they are often used for convenience with part of the thread exposed to the air and therefore generally at a lower temperature than that of the bulb. This introduces an error, but a correction can be applied as follows.

Suppose the temperature of the bulb is t_b, the mean temperature of the exposed part of the mercury thread is t_e, and the length of exposed mercury corresponds to n degrees on the scale. Had this exposed thread been heated to t_b also it would have expanded an additional number of scale divisions given by $n \times (t_b - t_e) \times \alpha$, where α is the apparent coefficient of expansion of mercury in glass, which is usually taken as 0·00016. In practice t_b is not known directly, but the uncorrected reading of the thermometer (t) is near enough; t_e is usually taken as the temperature registered by a thermometer with its bulb placed alongside the middle of the exposed stem. Then the corrected temperature is given by

$$t_{\text{corr.}} = t + 0·00016n(t - t_e)$$

t = uncorrected reading: n = no. of degrees exposed: t_e = exposed thread temperature.

Emergent stem corrections may be considerable, particularly with high temperature thermometers, e.g. 20° at 400° C. The correction should always be applied wherever it would have a significant effect on the result.

Thermocouples. Thermocouples are readily constructed from the appropriate wires by soldering (copper-constantan) or melting in oxy-coal gas flame. Fig. 3.1 shows schematically two methods of measuring temperatures with a thermocouple. In (a) the couple is simply connected by copper leads to an accurate millivoltmeter, and the steady deflection of the needle is observed. In this arrangement the cold junction is somewhat indefinite, being at the point A where the copper leads are joined to the thermocouple wires. Also, the deflection of the millivoltmeter is dependent on its internal resistance and on the resistance of the leads. An accuracy of about 3° on 1,000° is obtainable.

Arrangement (b) is used where higher accuracy is needed. The "cold junction" is made in a separate vessel, the temperature of

which is measured with a thermometer; alternatively, a Dewar vessel with melting ice may be used. The e.m.f. generated by the thermocouple is determined by means of a sensitive potentiometer *P* similar in principle to that described for measuring the e.m.f. of voltaic cells (see pp. 247–9). A common type of portable thermo-couple potentiometer is sensitive to about 0·01 mV and has a range up to 100 mV. This method, of course, determines the maximum (open circuit) e.m.f. of the couple, and is therefore independent of the resistance of the leads.
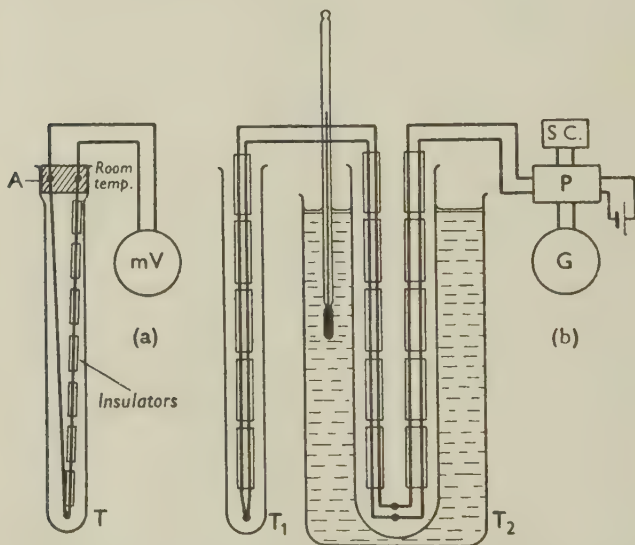
Fig. 3.1. Measurement of temperature by thermocouple (schematic). (a) Direct method, using millivoltmeter. (b) Precision potentiometric method, with "cold junction". (P, potentiometer: S.C., standard cell: G, galvanometer.)

The calibration tables for thermocouples are generally expressed as the e.m.f. generated by the couple when the "cold junction" is at 0° C. If, instead, the " cold junction " is at room temperature, the e.m.f. obtained is correspondingly diminished, and a correction —the "cold junction correction"—must be applied. Since the thermo-electric e.m.f. is not quite linear with temperature it is not accurate simply to add on the cold junction temperature. Instead, the e.m.f. generated by the cold junction is read from the tables, and this value is *added* to the observed e.m.f. to give the e.m.f. which would have been obtained had the cold junction been at 0° C. The corresponding temperature of the hot junction can then be read

from the calibration tables. Table A6 (p. 354) in the Appendix gives typical e.m.f.-temperature tables for copper-constantan, chromel-alumel, and platinum/13% rhodium-platinum couples.

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Weissberger, Vol. 1, Pt. 1, Ch. 1.
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Roberts, *Heat and Thermodynamics*, Ch. 1, 4th edn., 1951 (Blackie and Son, London).
Griffiths, *Methods of Measuring Temperature*, 3rd edn., 1947 (Griffin, London).
[1] Trav. Bur. Int. Poids Mes., 1934, Vol. **19**, *or*: *The Units and Standards of Measurements employed by the National Physical Laboratory* (H.M. Stationery Office, London).
[2] Stimson, *J. Res. Nat. Bur. Standards*, 1949, **42**, 209 (R.P. No. 1962).
[3] See monographs cited above.
[4] Platinum thermocouples guaranteed accurate to 1° at 1,000° C are supplied by Messrs. Johnson, Matthey and Co., Hatton Garden, London.

3B. TEMPERATURE CONTROL—THERMOSTATS

As most of the properties studied in physical chemistry are affected by temperature, it is very important to have means whereby experiments can be carried out at constant temperature. Constant temperature baths, or *thermostats*, are therefore an essential part of the equipment of a laboratory for physical chemistry.

A useful range of fixed temperatures can be obtained by employing baths immersed in boiling liquids, melting solids, or salts at their cryohydric or transition temperatures (see Tables A1, A2, A3, in the Appendix). However, heated thermostat baths with automatic temperature control are more versatile and are indispensable when a constant

FIG. 3.2. Components of a constant temperature bath (schematic).

A, tank: B, bath liquid: C, stirrer: D, electric motor: E, heater: F, thermoregulator: G, relay: H, thermometer.

temperature must be maintained over a long period. Innumerable methods have been devised for producing constant temperature; in this section a number of more commonly used pieces of apparatus will be described.

The usual components of a thermostat are shown diagrammatically in Fig. 3.2.

Thermostat baths. The tank *A* may be of metal (copper, galvanized or enamelled iron) but glass (e.g. Pyrex) is better for a small
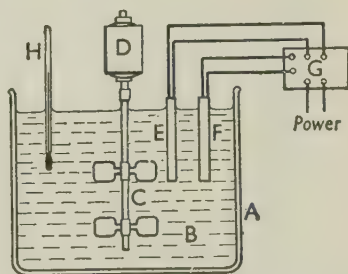
thermostat. If readings must be made of immersed instruments such as manometers, one or more sides must be constructed of plate glass. Water is most often used as the bath liquid B; to prevent micro-biological growth a muslin bag containing mercuric chloride may be suspended in the water. For temperatures above about $40°$ C evaporation becomes serious, and a layer of liquid paraffin is sometimes poured on the water. Alternatively, the water level may be maintained by an ordinary constant-level device. If the tank is of glass it is then necessary to connect the constant-level tube via a syphon fitted with an air-trap as in Fig. 3.3. Air bubbles released from the water rise into the trap instead of breaking the syphon, and the air collected there may be removed occasionally by sucking through the tube G.
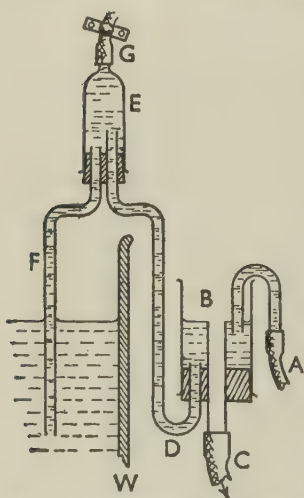
For temperatures between about $80°$ and $300°$ C a high-boiling liquid paraffin oil is generally used as bath liquid. At still higher temperatures molten salts or liquid metals (tin, lead) may be used, but wherever possible the liquid is dispensed with, and the object to be heated is simply placed in a furnace which is maintained at constant temperature (see below).

As liquids such as water are poor conductors of heat it is important to stir the bath liquid of a thermostat vigorously to maintain uniformity of temperature. A metal paddle stirrer C driven by a small electric motor D is generally employed. A large-bladed paddle driven relatively slowly—as, for example, by a gramophone turn-table motor—is more satisfactory than a small stirrer driven at high speed. Small baths can be stirred by a stream of bubbles of air or other gas from a submerged jet.

FIG. 3.3. Constant-level device for thermostat bath.

Temperature regulation. To maintain a thermostat at a temperature above that of the surroundings, heat must be added to counteract that lost by radiation, evaporation, etc. Gas heating may be used for simplicity, but electric heating is preferable, and may be provided by metal immersion heaters (such as those used in small electric kettles), or glass heating lamps, or simply a helix of nichrome wire in a length of Pyrex glass tubing bent into the shape of a "U". In order to obtain automatic regulation of the temperature, a *thermo-*

regulator is immersed in the bath, its function being to switch on the heating when the temperature falls below the required value and switch it off again as soon as the required temperature is restored. It is an advantage to have two heaters, one of which can be left on constantly to supply almost enough heat to counteract losses, while the other is switched on and off by the thermo-regulator. By this means the fluctuations of the temperature of the bath can be reduced. When a metal immersion heater is used, it is a convenience to connect a small indicator lamp (e.g. 5-watt neon bulb) in parallel with the heater to show when the latter is on.

While many types of thermo-regulator have been devised and many find use in industry, only a selection of the types most useful in the laboratory will be described here. Most laboratory thermo-regulators are not capable of controlling more than a small power, and they must therefore be used in conjunction with some type of *relay* G (see below).

The most robust type of regulator depends on the expansion of a bimetallic helix. Since the inner and outer metals of the helix expand to different extents a torsional movement is produced. This principle is used in the Sunvic thermostat (Fig. 3.4) to open or close electrical contacts. The bimetal strip *A* may be immersed directly in water or be protected by a sheath. The operating temperature can be altered by rotating a knob *B* which moves the "fixed" contact; for example, a range of $\pm 7°$ can be covered by one instrument having a sensitivity of $\pm 0.1° \text{C}$. The contacts are rated to carry up to 0.1 amp only, and are therefore used with hot-wire or electronic relays (see below).

Fig. 3.4. Sunvic bimetallic thermo-regulator. (Courtesy Messrs. Sunvic Controls, Ltd., London.)

For controlling a thermostat to better than $\pm 0.1°$, liquid expansion regulators are generally used. The toluene-mercury type, such as that shown in Fig. 3·5, is most often employed in physical chemistry. The bulb *A* is filled with toluene (chosen for its high coefficient of expansion and fairly high boiling point) while the bend of the tube and the narrow upright tube *B* are filled with mercury. The upper end of the tube *B* is of small bore (*c.* 2 mm) to increase the sensitivity of the regulator, giving a relatively large rise and fall of the meniscus for a change of volume of the toluene. Electrical contact is made with the mercury by a platinum wire *C* sealed

through the wall of the tube B and a steel needle D which can be raised or lowered in the narrow part of B by means of a screw. The side-arm E with stopcock is to facilitate introduction or removal of mercury when adjusting the temperature at which the regulator operates. Fine adjustment of the operating temperature is obtained by movement 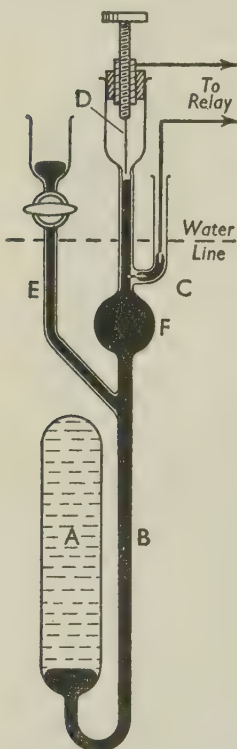of the contact D. The bulb F is to prevent air entering the side arm E in case the regulator is ever cooled much below its usual operating temperature—as when the thermostat is out of use. (If this were to occur, the regulator would have to be adjusted afresh).

The operation of the regulator is simple; as the temperature increases the toluene expands and the mercury rises until it makes contact with D, thus closing an external circuit containing a relay by which the heating is switched off. The sensitivity of such a regulator is about $\pm 0.01°$.

Filling. Toluene-mercury regulators often surprisingly difficult to fill, particularly if the tube B is narrow. It is worth fitting up an arrangement by which the regulator can be evacuated and toluene can be introduced with the regulator tilted in any desired position so that the last bubbles of air can be removed from the bulb A. (The toluene should have been previously dried and distilled.) Next, clean, dry mercury is poured into B, and allowed to displace some of the toluene from A. The excess toluene must be removed by a pipette and filter paper, and then the remainder of the regulator is filled with mercury. Finally, the regulator must be immersed in a water-bath and brought to the temperature at which it is required to operate, and the mercury level must be adjusted until it stands at a con-

FIG. 3.5. Construction of a toluene-mercury thermo-regulator.

venient level in the narrow part of the tube. The final adjustment can be made by trial by screwing the contact D up or down when the regulator is actually in use, until a position is found at which the make-and-break of the contact occurs at precisely the required temperature.

A thermo-regulator, more convenient to use and more sensitive in its action than that represented by Fig. 3.5, has been devised by Jelinek.[1] The upper part of this regulator which, when in use, is immersed in the bath liquid, is shown in Fig. 3.6 (a), from which its action will be readily understood. In place of toluene, paraffin oil

(medicinal paraffin), contained in a branched bulb of about 150 ml capacity, is used as regulating liquid and fills also the upper part of the regulator above the mercury. While the regulator is being adjusted for temperature, tap C is kept open so that oil can expand into A without affecting the level of the mercury; and when the desired temperature is reached, tap C is closed. Rise of temperature and expansion of the paraffin oil then cause the mercury to make contact with the steel needle at D. The circuit through the relay is thereby closed and the heating current interrupted. The adjustment of this regulator for different temperatures is rendered very simple by means of the tap C, and the complete immersion of the regulator in the bath liquid renders its functioning independent of the surrounding atmospheric temperature.
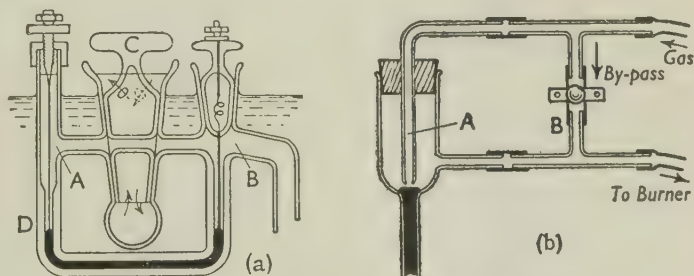

FIG. 3.6. Alternative heads for toluene-mercury thermo-regulators (compare Fig. 3.5).

(a) Improved means of adjusting operating temperature of electrical regulator.
(b) Control device for gas-heated thermostat.

In place of electrical control of temperature, one may use gas heating and a toluene-mercury regulator similar to that shown in Fig. 3.5 can be modified at the upper end as in Fig. 3.6 (b). The flow of gas through the jet A is reduced and finally stopped as the mercury rises. A by-pass gas stream flows through B and is controlled by a screw-clip to give a flame which is just insufficient to maintain the thermostat at the required temperature. Consequently the regulator is not called upon to control a large flow of gas, and, further, the flame is not extinguished when the flow through the jet is cut off. A micro-burner is a convenient heater for a small thermostat, and a bunsen burner with gauze cap and a separate pilot jet is suitable for a tank which has to be heated above about 30° C. It is advisable to use flexible metal pipes for connecting gas thermostats to reduce the risk of fires which might arise through the perishing of rubber tubing.

Sometimes one needs three or four different constant temperatures —for example, when studying the influence of temperature on the

velocity of a chemical reaction (Ch. 13). For such purposes, the simple vapour-pressure gas thermo-regulator shown in Fig.3.7 can be used to control the temperature of a large beaker to within $\pm 0 \cdot 1 °$ C. The liquid in the bulb is chosen to have a boiling point at about the required temperature (e.g. ether 35°, methylamine 46°,
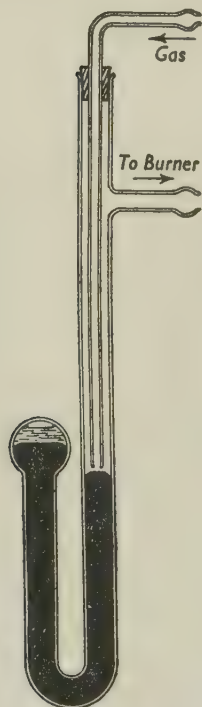

FIG. 3.7. Vapour-pressure
thermo-regulator for gas
heating.
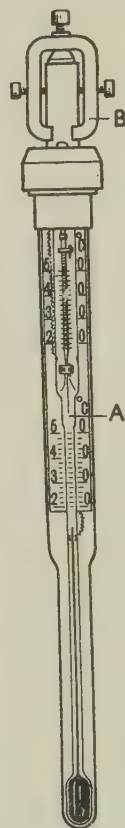

FIG. 3.8. Adjustable contact
thermometer.
(Courtesy Messrs. Electro Methods,
Ltd., Stevenage, Herts.)

acetone 56°, chloroform 66°, carbon tetrachloride 76°, triethylamine 89°). When the boiling point of the liquid is reached, a large expansion occurs owing to vaporization of the liquid in the bulb, and the gas flow is cut off. The boiling point of a liquid varies slightly, of course, with the barometric pressure and hence the regulator will not always give exactly the same temperature from day to day. A

small adjustment of temperature can be obtained by altering the level of mercury in the open limb of the regulator in order to vary the pressure exerted on the volatile liquid.

For some purposes—notably, when a property such as the vapour pressure of a liquid is to be measured accurately at a number of different temperatures in succession—it is an advantage to use an electrical regulator (for convenience of adjustment) in conjunction with a gas heater (for rapid heating). A special electro-magnetically operated gas valve can be obtained for this purpose.[2]

Undoubtedly the most convenient type of thermo-regulator for use when the thermostat temperature has to be changed frequently is the adjustable contact thermometer (Fig. 3.8). This consists of a mercury thermometer having a large bulb and a fine contact wire A which can be raised or lowered inside the sealed capillary tube by rotating an external magnet B. There is a marker on an upper auxiliary scale which indicates the approximate temperature at which the regulator will operate, and it therefore takes only a few moments to adjust the apparatus to any required temperature within the range covered by the particular thermometer. Since contact thermo-meters are delicate and expensive, they should be mounted in a metal tube for protection; a cut-away part of the tube permits the scale to be read. Also, it is absolutely essential that only minute currents should be passed through them. Consequently a sensitive relay operating with only a milliampere or less must be employed with them. Of course, an ordinary toluene-mercury regulator can be adapted in place of a sealed contact thermometer by providing a long capillary and movable contact point, the setting of which can be previously calibrated.

Relays. The electrical contacts in mercury thermo-regulators are not capable of handling currents large enough to heat a thermostat directly, and therefore some type of relay is necessary. Furthermore, the relay should be sensitive so that only a very small current has to be broken by the regulator, otherwise sparking at the mercury surface quickly fouls the meniscus by oxidation and renders the make-and-break unreliable. The spark can be reduced by connecting a con-denser (e.g. 0·1 μF, paper, 6,000 V working) across the gap or across the solenoid. Alternatively, a regulator can be sealed with a small pressure of hydrogen in it to prevent oxidation. In any case, the smaller the current to be carried by the contacts, the more satisfactory will be the operation of the thermo-regulator. A number of useful types of relay are described below.

Fig. 3.9 shows a simple electro-magnetic relay of the "Post Office" type; various designs are obtainable relatively cheaply. Such relays are wired to take about 6–12, 24, or 230 V d.c. in the

solenoid, and this may be supplied either from dry cells or by stepping down the mains with a series resistance R or potential divider of appropriate value to give the required p.d. across the relay solenoid.   The minimum effective voltage should be found by trial. Relays can be obtained with coil resistances ranging from about 100 to 10,000 Ω; the higher the resistance, of course, the smaller the current needed (i.e. 100–1 mA respectively) but the more sensitive patterns are correspondingly less robust and the contacts are lighter. Robust relays need about 4 watts to operate them.   The relay contacts handle 0·1–1 amp according to type.   "Microwatt" relays operating on less than 1 mA can be obtained.

It is possible to couple two relays together: a sensitive one can be operated by a very small current from the regulator, and the current obtained from the first relay can be made to actuate the second (robust) relay capable of handling a large current.

The operation of the electromagnetic relay is easily followed from Fig. 3.9. When contact is made in the thermo-regulator, current passes through the solenoid A which attracts the iron disc B. The lever arm C hinges about the fulcrum D and forces the spring contact points E,E apart, thus breaking the current in the heater circuit.
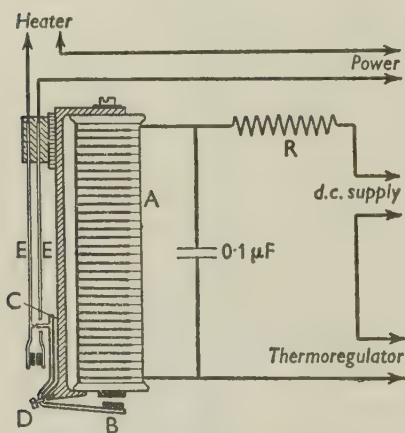

FIG. 3.9. "Post Office" relay (wiring diagram).

An improvement on the "Post Office" type of relay is a pattern in which a sealed mercury switch takes the place of metal contact points.   Fig. 3.10 (a) shows a tilting mercury switch relay and Fig. 3.10 (b) a stationary mercury relay.   Typical operating characteristics are: type (a) requires about 4 VA, and switches about 1 kW; type (b) operates with about 2 VA, switching up to 1·5 kW.

A very reliable type of relay for use with bimetallic or toluene-mercury regulators is the vacuum hot-wire switch.   The principle of operation is illustrated by Fig. 3.11 (a) and the construction by Fig. 3.11 (b).   When the regulator contacts are open current passes through the wire W which then expands, allowing the lever C to deflect and thus bringing the main contact points G together so that current can pass in the heat circuit.   When the regulator contacts

close they short-circuit the heater, and consequently the bimetallic strip cools, and, in a few seconds, the contact points open, thus breaking the circuit. Hot-wire switches are made for various voltages and in various sizes; a suitable relay for thermostats is one handling up to 2 kW, and operated by a current of about 20 mA through the thermo-regulator.

Precision control of temperature. The methods described above are adequate to maintain a thermostat bath at constant temperature to within ±0·01° C. For still better control attention must be paid to the following points. (1) Very efficient stirring is essential. (2) Heat losses must be reduced by insulation. (3) The heater (or, better, heaters) should be of large area but small heat capacity to reduce lag. (4) The thermo-regulator should be of large volume but of such a form that it presents
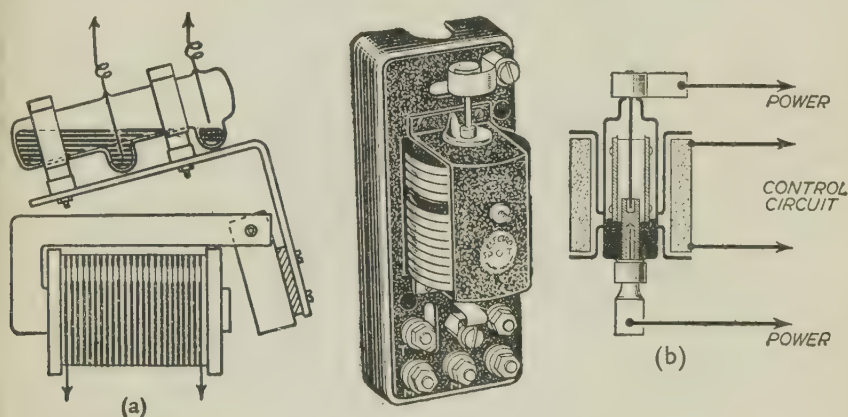

FIG. 3.10. Electromagnetic mercury relays.
(a) Tilting pattern. (b) Stationary pattern.

a large surface area in contact with the bath fluid. (5) The capillary in which the mercury rises should be as narrow as practicable in order to enhance sensitivity. (6) To reduce fouling of the mercury, a steel needle should be used for contact (since steel is not wetted by mercury) and the current controlled by the contact should be kept very small—preferably less than 1 mA. For this purpose it is best to employ an electronic (valve) relay.

Electronic relay. The essential characteristic of a triode thermionic valve is that the main current passed through the valve between cathode and anode can be controlled by relatively small changes of potential of the grid, and the current drawn from the grid is minute compared with that which it controls. Fig. 3.12 gives a circuit diagram for a simple electronic relay suitable for operating a mercury switch or hot-wire vacuum switch. Any valve capable of passing a fairly heavy anode current is suitable—for

example, an output pentode such as Mullard EL33, or "beam tetrodes" such as Osram KT63 or KT66 (American types 6V6, 6L6), which will pass 40–50 mA when used as a triode, the screens being connected to the anode.   When the regulator contacts are open, the grid is strongly negative and negligible anode current passes, but when the contacts are closed the grid potential becomes approximately zero and the full anode current
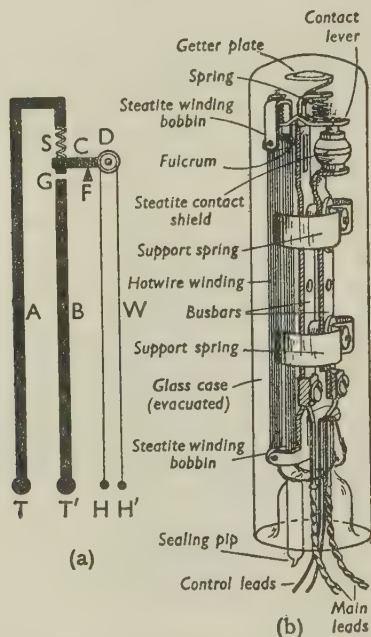

Fig. 3.11. Sunvic vacuum hot-wire switch.
(a) Principle of operation (schematic). (b) Constructional details.
(Courtesy Messrs. Sunvic Controls, Ltd., London.)

flows through the valve and through the relay coil.   Forty mA at about 100 V is sufficient power to operate a relay switching 1 kW.   With this electronic relay it is necessary to arrange that the thermostat heater is *on* when no current passes through the relay.   The valve takes negligible grid current—only a few microamperes.

Increased precision can be obtained from a toluene-mercury regulator by arranging for the contact wire to rise and fall slowly through about 1 mm in the capillary tube above the mercury meniscus.   The result is that the *duration* of the period of electrical contact between the mercury and the wire becomes a function of the difference between the bath temperature and the temperature at which the thermostat is required to operate. Thus, when the bath temperature is much too low the period of contact (during which the heater is off) is short or nil, whereas when the required

temperature is almost reached, the heater is off for progressively longer periods. This gives a *gradual* reduction of heating—the so-called "proportional control"—instead of the ordinary on-off regulation. The latter suffers from the disadvantage that the temperature necessarily fluctuates over a certain range above and below the required temperature owing to "lag". Movement of the contact can be effected by an accessory known as a "proportioning head" (Sunvic Controls, Ltd.) in which the movement is produced by deflection of an electrically heated bimetallic strip. This apparatus, used in conjunction with an electronic relay, has made it relatively easy to achieve temperature control to ±0·001° C.
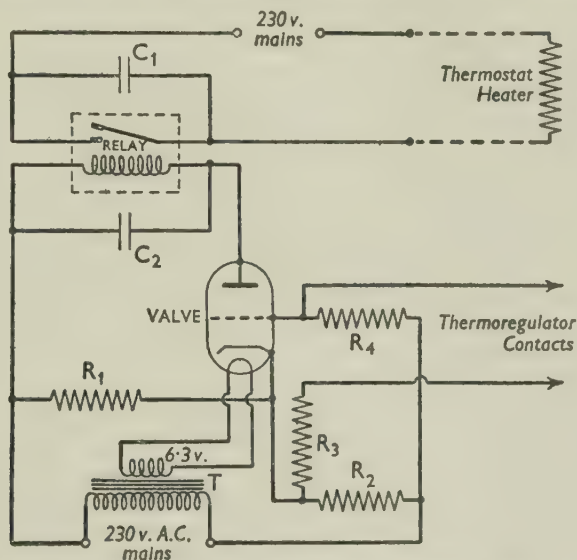

FIG. 3.12. Circuit diagram of simple electronic relay.
Components: $R_1 = 17,000\,\Omega$, 5 watt; $R_2 = 3,000\,\Omega$, 5 watt; $R_3 = 75,000\,\Omega$; $R_4 = 5$ megΩ; $C_1 = 0\cdot1\,\mu$F; $C_2 = 1\,\mu$F. Relay, $1,000\,\Omega$ coil, heavy duty contacts. Valve, KT63.)

Circulation of water. The maintenance of a constant temperature in an apparatus outside the thermostat (e.g. a refractometer) is effected by circulating water from the thermostat by means of a pump. The small electrically-driven centrifugal pumps used for garden fountains are suitable provided the apparatus is placed on the suction side of the pump so that it receives water direct from the thermostat rather than water which has passed through the pump where its temperature may be altered. Centrifugal pumps, of course, need "priming". In the absence of a pump, it is possible to obtain a stream of water at constant temperature by flowing tap-water slowly through a large metal coil immersed in a thermostat of adequate heating capacity.

Temperatures below that of the surroundings. Regulators have been designed which will switch on a source of cooling when the temperature of a thermostat bath rises above the temperature required. It is simpler, however, to provide a constant amount of cooling and to supplement this with intermittent heating controlled by a normal thermo-regulator such as one of those described previously. Cooling can be effected conveniently by flowing tap-water or ice-cold water through a coil of lead or copper immersed in the thermostat, the water being run to waste afterwards. When the bath temperature falls too low, the thermo-regulator switches on the supplementary heater. The flow of the cooling water can be regulated so that the heater operates only occasionally.

For temperatures somewhat below the freezing point of water, the bath liquid or liquid in the cooling coils may be a concentrated solution of calcium chloride or of ethylene glycol, and the cooling can conveniently be obtained by a small refrigerator unit.

Temperatures between $0°$ and $-78°$ C can be produced by adding solid carbon dioxide to a bath of alcohol, acetone, or ether contained in a Dewar (Thermos) vessel. For still lower temperatures pentane cooled by liquid air can be used, and, if necessary, a low-temperature thermostat ("cryostat") can be constructed in which quantities of liquid air are delivered automatically to a pentane bath by a special thermoregulator.[3]

Freezing mixtures from ice. The melting point of ice is lowered by addition of a solute to the liquid (Ch. 6). Consequently, if powdered ice is added to say, brine, some of the ice melts and the temperature falls below $0°$ C. With very soluble salts it is possible to reach temperatures even below $-50°$ C (e.g. $-51°$ with $CaCl_2.6H_2O$) but such mixtures, of course, have little reserve cooling power left. With moderately soluble salts, however, a useful and stable temperature is obtained by adding excess of the salt to powdered ice in order to produce the eutectic ("cryohydric") mixture of ice+salt+saturated solution. For common salt, for example, this temperature is $-21°$ C and a number of other cryohydric temperatures for readily available substances are shown in Table A3. Such freezing mixtures will hold a steady temperature as long as any ice remains unmelted, whereas ice+unsaturated brine mixtures slowly rise in temperature as the solution becomes diluted by the melting ice.

Freezing mixtures from solid CO_2. The temperature of solid carbon dioxide when its sublimation pressure is 1 atmosphere is $-78°$ C, and this is therefore the normal temperature assumed by the solid, but it varies slightly, of course, with the barometric pressure. Lower temperatures can be obtained by means of reduced pressure. Low temperature baths are prepared by cooling a liquid

(f.p. below $-78°$ C) with powdered carbon dioxide; alcohol (methylated spirits) is generally used. Lumps of carbon dioxide are wrapped in a cloth and smashed with a hammer, and the powder is added little by little to a thermos flask half full of alcohol which is stirred with a stiff copper wire or glass rod stirrer. If too much carbon dioxide is added at a time, the effervescence causes the liquid to overflow. Eventually a point is reached when excess carbon dioxide remains in suspension and the bath is then at $-78°$ C. If it is to be kept at this temperature a considerable excess of powdered carbon dioxide can now be stirred in, and further quantities can be added from time to time as required. Temperatures between $-78°$ and room temperature can, of course, be obtained by using less carbon dioxide in the first place, but such baths will not hold a steady temperature. Instead it is better to use the carbon dioxide to freeze (partially) a pure organic liquid of suitable freezing point, as the solid-liquid equilibrium produces a constant temperature, heat conducted into the bath being taken up as the latent heat of fusion of some of the solid. Suitable liquids and their freezing points are listed in Table A1 (p. 351).

Temperatures in the range 300–1,000° C. Above 300° C liquid baths become inconvenient. A number of fixed constant temperatures can be obtained by means of boiling liquids such as mercury and sulphur, but the most convenient form of heating is the electric resistance furnace. Such furnaces can be made readily in the laboratory (Fig. 3.13). The heating element A consists of nichrome resistance wire and this is wound on a tube or other support B of "Pyrex", fused silica, refractory fireclay, mullite, or even iron. In the last case, the winding must be insulated from the iron by several layers of asbestos paper, applied moist. The nichrome wire should be spaced evenly to avoid local over-heating, but it is an advantage gradually to decrease the spacing of the turns towards the ends of the heated zone in order to counteract the cooling effect of the ends and thus improve the degree of uniformity of temperature along the tube. The ends of the wire are secured on the tube, and connected by treble-thickness leads to the terminals T,T. The windings should be held in position by application of a thin layer of alundum cement C (Thermal Syndicate, Ltd.). Finally, the heater should be lagged by a layer of asbestos string, kieselguhr or calcined alumina powder D. The thicker the lagging, the less sensitive will the furnace be to draughts, etc., but the longer it will need to reach a steady temperature. A well-lagged tube furnace with an element 1 ft long of diameter about $\frac{1}{2}$ in needs only about half a kilowatt to reach 1,000° C; for larger sizes, the power increases approximately as the area of the heated surface.

The temperature of the furnace can be adjusted by means of a large sliding rheostat R connected in series with the furnace winding. If the furnace is run from a.c. mains, the current can be regulated conveniently with a variable auto-transformer such as the "Variac" regulating transformers, supplied by the Zenith Electric Co., Ltd., Villiers Road, London, N.W.2, which is less wasteful of power than a rheostat. However, a simple "energy regulator" (Sunvic Controls, Ltd.) offers advantages over either rheostat or auto-transformer as it is neither wasteful nor expensive and largely compensates for
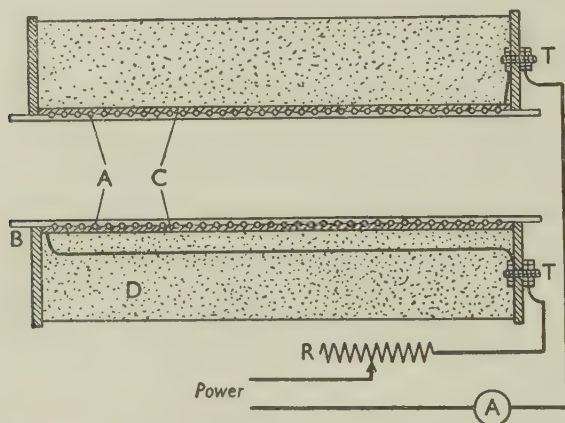

FIG. 3.13. Construction of nichrome-wound electric furnace.

variations in the mains voltage. The principle of this device is that a small heater element warms a bimetallic strip which then deflects and opens a contact, thus breaking the circuit, until the strip cools again. The frequency of the on-off movement and the proportion of time spent in the "on" position therefore depends on the power passing in the circuit and the setting of the contact points. A simple type of energy regulator known as the "Simmerstat" (Sunvic Controls, Ltd.) which is used to give continuous control of hot-plate temperatures in electric cookers, will maintain the temperature of a small furnace constant to within two or three degrees at temperatures in the region of 1,000° C. The setting of the energy regulator must be found by trial; also, the ambient temperature should be steady so that heat losses are constant.

For more precise control of furnace temperatures it is necessary to use rather elaborate amplifier circuits based on electrical resistance thermometers or thermocouples.[4]

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[1] Jelinek, *Bull. Soc. Chim.*, 1937 (v), **4**, 1811.
[2] Supplied by Messrs. Electro Methods, Ltd., Stevenage, Herts.
[3] Griffiths, *op. cit.*, Ch. 16.
[4] Refer to any of the monographs cited above.

DENSITY OF GASES AND VAPOURS

Determinations of the density of gases and vapours have played an important part in the history of chemistry because the molecular weight of a substance in the gaseous state at the temperature of vaporization can be calculated from its density. Although this method of determining molecular weight is less needed nowadays than formerly, it still forms the basis of an important method of determining atomic weights accurately. The determination also has other applications—for example, the analysis of gas mixtures,[1] and the study of chemical dissociation (see pp. 63–5).

4A. GAS DENSITY

The *absolute* density of a gas is the mass of unit volume, i.e. 1 litre or 1 ml, at the stated temperature and pressure. The *standard* density is the absolute density at 0° C and 1 atmosphere pressure (i.e. the pressure exerted by a column of mercury 760 mm high at 0° C and at sea-level in latitude 45°). In connection with molecular weight determinations, *relative* gas densities are often used; these are the ratio of the density of the gas to that of a reference gas—usually hydrogen or oxygen—at the same temperature and pressure. Since Avogadro's hypothesis states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, the relative gas density is equal to the ratio of the molecular weights of the two gases. Oxygen is taken as the standard for the chemical scale of atomic weights, its molecular weight being defined as 32·000, and hence the molecular weight of another gas follows from its density relative to that of oxygen.

In practice, all gases deviate to some extent from the ideal gas law

$$PV = \frac{m}{M}RT$$

(where P is the pressure, V the volume, m the mass, M the molecular weight, R the gas constant, and T the absolute temperature). Consequently, Avogadro's hypothesis is not *accurately* correct under ordinary conditions, nor would 1 g molecular weight ("1 mole") of every gas occupy at S.T.P. *exactly* 22·414 litres, which is the volume

occupied by an ideal gas under these conditions. Ordinary gases
such as O_2, N_2, H_2, etc. deviate by less than 1% from the ideal gas
law at 1 atmosphere pressure, but easily condensible gases such as CO_2
and NO_2, and, above all, *vapours* (i.e. gases at temperatures below
their critical temperature) show considerable deviations. Conse-
quently, normal gas or vapour densities give only approximate values
of molecular weights. Where the highest accuracy is required, as
in atomic weight work, either a more accurate equation of state is
employed (for example, the van der Waals equation) or, better, use
is made of the fact that deviations from the ideal gas law diminish
as the pressure is reduced. Thus, in the "method of limiting
densities" the relative density of the gas compared with oxygen is
determined at a series of different pressures, and the value for zero
pressure is obtained by extrapolation. This method eliminates all
errors due to non-ideality of the gases.

Methods of determination of gas density. The oldest and still the
most convenient method of determining the density of a gas is to
weigh it in a globe of known volume (Regnault, 1847). With
proper precautions a very high accuracy can be achieved, as in the
classic work of Lord Rayleigh [2] which led to the discovery of the
inert gases.

The chief difficulties encountered in Regnault's method arise from
the necessity of weighing large glass vessels (see below). This
operation can be avoided if the gas can be weighed in some con-
densed form either before or after its pressure is measured at con-
trolled temperature in a large vessel of known volume. For example,
the weight of a considerable volume of CO_2 could be obtained from
the loss of weight of a sample of pure calcite from which the gas was
obtained by heating. Alternatively, the CO_2 could be absorbed
and weighed in a soda-lime tube. In the hands of the modern
Spanish chemist, Moles, an accuracy approaching 1 in 10^5 has been
achieved with this "*volumeter method*".[3]

A third method employs the *gas buoyancy micro-balance*, which
depends on the principle of Archimedes. The apparatus usually
takes the form of a small closed silica bulb which is attached to one
arm of a light torsion- or other micro-balance, the whole apparatus
being enclosed in a vessel to which the gas can be admitted. The
buoyancy of the bulb depends on the density, and hence pressure,
of the gas. The pressure (p_A) is found at which the pointer of the
micro-balance coincides with some arbitrary mark, and the gas is
then replaced by a reference gas (usually oxygen); the pressure is
again adjusted until the same position of the balance is restored. A
different pressure (p_B) is, of course, required, but the density of the
first gas at pressure p_A must be equal to the density of the reference

gas at pressure p_B. This gives the required gas density, assuming the ideal gas law to be applicable since

$$\frac{\text{standard density of gas } A}{\text{standard density of gas } B} = \frac{\text{pressure of gas } B}{\text{pressure of gas } A}$$

Alternatively, the method of limiting densities may be employed for accurate determination of molecular weights.[4]

EXPERIMENT

Determine the absolute density of carbon dioxide (or dry air) by the globe method.

The glass globe for this determination (Fig. 4.1) should have a volume of about 500 ml, and carry a glass stopcock preferably of the hollow-key type used for vacuum work.   The stopcock should be close to the bulb and attached by fairly stout-walled tubing to reduce danger of breakage; also, the end of the tube may be drawn out a little to facilitate attachment and removal of rubber pressure tubing.

The first step is to determine the volume of the globe. This is obtained by weighing it evacuated and then full of water. It is first evacuated by means of an oil or water pump and then weighed. The tap is then opened while the end of the tube dips under the surface of a quantity of recently boiled distilled water. When the globe is full, it is placed in a water-bath, the tap being left open until the globe has taken the temperature of the bath, which is noted.   The tap is then closed so that its bore remains full of water, and the tube above the tap is dried by means of filter paper.   The globe is weighed to 0·01 g on a large balance.   The difference between the weight of the exhausted globe and that of the globe full of water gives the true weight of the water since the buoyancy acting on the globe is the same for both weighings and the buoyancy correction for the brass weights is negligible in the present instance (density of brass = 8·4; density of dry air at 20° C = 0·0012).   The density of water at the temperature at which the globe was filled is read from Table A4, p. 353), and hence the volume of the globe is calculated.

Next, the globe is emptied by taking out the key of the tap and removing the water by a narrow glass jet connected with a filter pump.   It is a good plan to remove grease from the tap at this stage and scrupulously clean the globe inside and outside with chromic acid mixture followed by plenty of distilled water.   Thereafter the globe itself should not be handled by the fingers, but always with a

FIG. 4.1. Gas density globe.

clean chamois leather cloth or held by a piece of stout copper wire which is attached to the tap and bent to form a hook by which the globe can be hung on the balance.   The inside of the globe is dried by rinsing several times with alcohol and then with ether, the last drops of ether being removed by repeated evacuation at a water-pump. The key of the tap is given a *thin* smear of apiezon vacuum grease, and the globe is then ready for the main determination.
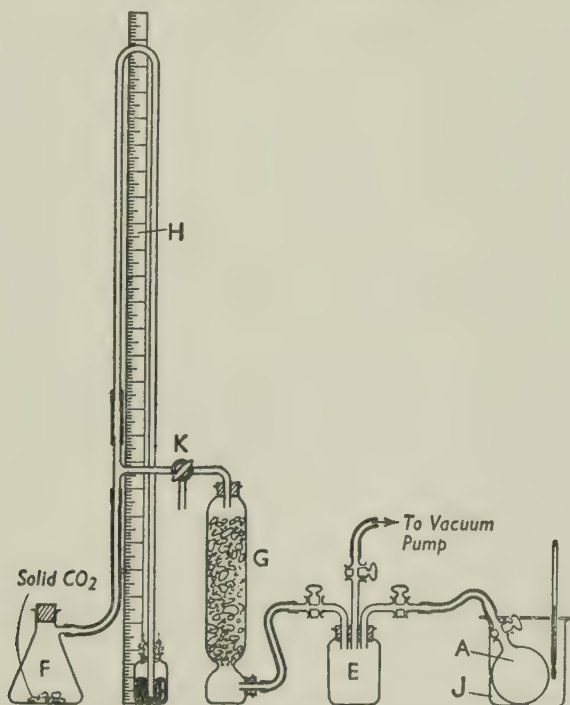

FIG. 4.2. Arrangement of apparatus for filling a globe with CO_2.

An arrangement such as that shown in Fig. 4.2 is convenient for filling the globe with carbon dioxide.   The mercury manometer H is intended to verify the degree of vacuum produced by the pump and to act as a safety valve from which excess pressure of gas can escape.   It also serves as an indicator of the presence of any leakages in the apparatus.   If present, these must be located and dealt with before proceeding with the determination.

The globe A is evacuated to the best vacuum obtainable and then weighed as accurately as possible after it has been wiped with the chamois leather and has stood long enough in the balance case to

reach thermal equilibrium. (Any leakage of the stopcock will be detected by a gradual increase of weight.) If the density of the atmosphere were to remain constant throughout the determinations, clearly no buoyancy corrections would be needed since the buoyancy of the globe would remain the same whether the latter were empty or contained gas. However, since it may be necessary to use weighings made on different days and therefore possibly subject to different buoyancy corrections and since the correction is not very accurate because the humidity as well as the pressure influences the atmospheric density, it is usual in this type of work to eliminate buoyancy corrections by using a counterpoise globe of about the same size as the one in which the gas is to be weighed. If the counterpoise globe is subjected to the same handling and wiping it also helps to reduce errors which might be introduced by variable amounts of adsorbed moisture on the surface of the glass.

The next step is to fill the globe with the gas at atmospheric pressure. If the density of dry air is to be determined, air is simply admitted slowly through a calcium chloride tube. If CO_2 is to be used, it may be prepared by a Kipp's apparatus, but is more conveniently obtained from a few pieces of solid CO_2 placed in a filter flask F which can be evacuated once or twice to remove air. CO_2 can also be obtained from a cylinder. However prepared, the gas should be dried by a small tower G of calcium chloride or silica gel, and the whole apparatus should be flushed through with CO_2 several times to remove air.

While the globe is being filled it can be kept in a cardboard or wooden box J, loosely wrapped in the chamois leather and with a thermometer in contact with it. This plan obviates difficulties of drying and temperature change which are incurred if the globe is placed in a water-bath, and it also saves time.

The globe is filled initially to a pressure slightly greater than atmospheric, but when sufficient time has been allowed for the temperature to become steady, the tap K is opened to the air for a few moments to allow the pressure in the globe to become equal to that of the atmosphere and the tap on the globe is then closed. The barometer is read. The globe is finally weighed again with the same precautions as before.

In order to determine the *reproducibility* of the measurements, the globe should be evacuated and weighed again; then filled with gas and weighed once more. These operations are probably the factors which limit the accuracy of the determination of gas density. As a check on the purity of the CO_2, a test may be made to see whether it is entirely absorbed by air-free potassium hydroxide solution. The bore of the tube beyond the tap should first be filled with the

solution and then the globe inverted and stood in the solution and the tap opened. If more than a small bubble of gas remains un-absorbed its volume can be estimated (e.g. by weighing the nearly full globe, filling and weighing again) and a correction applied on the assumption that it consists of air.

Calculation. If W is the weight of gas filling the globe, the volume of which has been calculated to be V ml, and if $t(^\circ$ C) is the temperature and p the barometric pressure in mm Hg (corrected for expansion of the scale and gravitational value (pp. 356–7) at which the globe was filled, then the volume (V_0) of the gas at standard temperature and pressure would be

$$V_0 = \frac{V \times 273 \times p}{(273+t) \times 760}$$ and its standard density $d = W/V_0$ and approximate

molecular weight $M' = (22,400 \times W)/V_0$.

It is of interest to calculate the effect on M of assuming the van der Waals equation of state to apply instead of the ideal gas equation, namely, for 1 mole of gas

$$(p+a/V^2)(V-b) = RT$$

The full equation, being cubic in V, is awkward to use, but on expansion, neglecting the very small term ab/V^2 and putting $a/V \approx ap/RT$, the equation simplifies to

$$pV = RT - p(a/RT - b)$$

This shows that for moderate pressures the deviation from Boyle's Law is linear, the term $(a/RT - b)$ being called the "compressibility coefficient" of the gas. The van der Waals constants, a and b, may be calculated approximately from the critical constants of the gas.

For CO_2, $a = 716 \times 10^{-5}$ and $b = 1,905 \times 10^{-6}$, the pressure being in atm. and the volume in (22·415 litres).

Hence, one can calculate the volume which 1 mole of CO_2 would occupy at the temperature and pressure of the experiment. The ratio of this calculated molar volume to the observed value must be equal to the ratio of the weight taken (W) to the true molecular weight, which can therefore be calculated.

Results. The results obtained for standard gas density should not differ by more than about 0·5% from the accepted values: viz. dry air, 1·2928 g per litre; CO_2, 1·9768 g per litre.

Degree of dissociation of a gas. Since the molecular composition of a dissociating gas varies with the temperature, the degree of dissociation and the dissociation constant at different temperatures, can be calculated from determinations of the density.

EXPERIMENT

Determine the density of nitrogen tetroxide at different temperatures.

In the Pyrex tube A (Fig. 4.3), place 8–10 g of roughly ground and well-dried lead nitrate. Connect the trap C, by means of the ground joint B, and open the tap D. The ground joint and tap may be

lubricated with phosphoric acid.   Exhaust the apparatus through the three-way tap E, and gently heat the tubes so as to get rid of moisture.   Place the trap C in a freezing-mixture of ice and salt and heat the lead nitrate, the three-way tap E being open to the air. Nitrogen tetroxide will be evolved and will condense in the trap.

When sufficient nitrogen tetroxide has been collected, close the tap D and disconnect the tube A.   The tube F is then connected by a ground joint with the globe G, which should have an internal volume of not less than about 500 ml.   The weight of the empty globe and its volume should previously have been determined as in the preceding experiment, a globe of similar size being used as a counterpoise.   Exhaust the globe through the tap E, and, after removing the trap from the freezing-mixture, allow nitrogen tetroxide to pass into the globe.   Exhaust and refill the globe with nitrogen tetroxide, and then place the globe in a freezing-mixture and collect 2–3 ml of
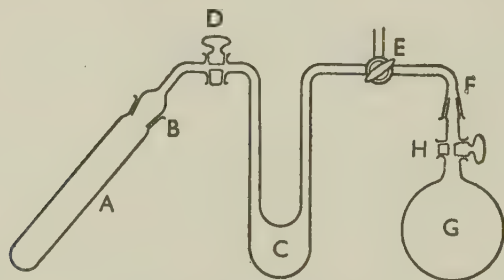

FIG. 4.3. Apparatus for preparing N_2O_4 and determining the density of the gas.

liquid nitrogen tetroxide in the globe.   Close the tap H and the three-way tap E, and disconnect the globe G.   This is then placed in a thermostat at a temperature of about 20°, the tap H being opened slightly so as to allow the excess of nitrogen tetroxide to escape, the escaping gas being passed through a tube of moist caustic potash. When all the liquid nitrogen tetroxide has evaporated, and gas ceases to escape from the globe, close the tap H, remove the globe from the thermostat, dry and weigh.   The barometric pressure should also be ascertained.

The globe with nitrogen tetroxide should then be placed in a bath at, say, 40°, and when it has taken the temperature of the bath, the tap H is slowly opened, so as to equalize the pressure, and then closed.   Dry and weigh as before.   Carry out similar determinations at, say, 60°, 80°, and 110°, using an oil bath.

At each temperature calculate the density of the gas and the apparent molecular weight.   It must be noted that at the higher

temperatures the volume of the globe must be corrected for the expansion of the glass. If V is the volume of the globe at temperature t, the volume at temperature t' will be $V[1+0.000025(t'-t)]$, where 0.000025 is the coefficient of cubical expansion of glass.

Calculations. As the temperature is raised, the N_2O_4 molecules dissociate into NO_2 molecules and at each temperature an equilibrium is established represented by $N_2O_4 \rightleftarrows 2NO_2$. The degree of dissociation at a given temperature can be calculated by means of the expression $\alpha = (d_t - d_0)/d_0$, where d_0 is the observed density and d_t is the density of the undissociated N_2O_4. Since the molecular weight is proportional to the density, $\alpha = (M_t - M_0)/M_0$, where M_t is the molecular weight of $N_2O_4(92)$, and M_0 is the apparent molecular weight of the gas at the given temperature.

If the total pressure (1 atm) of the equilibrium mixture is represented by P, the partial pressure of the N_2O_4 molecules will be given by $p_{N_2O_4} = \dfrac{1-\alpha}{1+\alpha} \cdot P$, and the partial pressure of the NO_2 molecules will be $p_{NO_2} = \dfrac{2\alpha}{1+\alpha} \cdot P$. The equilibrium constant K_p will be given by the expression

$$K_p = \left(\frac{2\alpha}{1+\alpha} \cdot P \right)^2 \Big/ \frac{1-\alpha}{1+\alpha} \cdot P = 4\alpha^2 P/(1-\alpha^2)$$

From the determinations of the density at different temperatures, one should calculate the value of α and the value of K_p. The values of log K_p for different temperatures should be plotted against $1/T$. From the curve so obtained, values of the equilibrium constant can be read off, and by applying the van't Hoff isochore in its integrated form,

$$\log_{10} \frac{K_1}{K_2} = \frac{-\Delta H}{2.303 \times 1.987} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

the value of $(-\Delta H)$, the heat evolved when the reaction takes place at constant pressure, can be calculated.

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[2] Rayleigh, *Proc. Roy. Soc.*, 1899, **55**, 340.
[3] e.g. Moles, Toral and Escribano, *Trans. Faraday Soc.*, 1939, **35**, 1439.
[4] e.g. Cady and Rarick, *J. Amer. Chem. Soc.*, 1941, **63**, 1357; Lambert and Phillips, *Phil. Trans. Roy. Soc.*, 1950 (A), **242**, 415.

4B. DETERMINATION OF VAPOUR DENSITY

The two well-known classic methods of determining the density of vapour of a substance which is liquid at normal temperatures are those of Dumas (1826) and of Victor Meyer (1882). The preceding experiment with N_2O_4 is essentially an application of Dumas's

method except that the bulb is closed with a stopcock instead of a glass seal. In Victor Meyer's method the vaporized liquid displaces air from a vessel maintained at a high constant temperature, but the volume of air is measured at ordinary temperatures. In some modifications of the method the volume is maintained constant and the increase of pressure is determined instead. Various forms of apparatus have been recommended, but only one will be described here.[1] The gas buoyancy micro-balance (suitably heated) can also be adapted to measure vapour densities.[2]

EXPERIMENT

Determine the density and molecular weight of acetone or chloroform vapour by Victor Meyer's method.

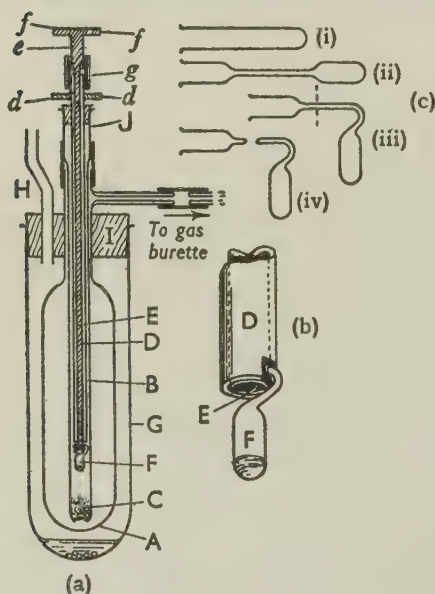Fig. 4.4 shows a form of apparatus[1] incorporating several improvements over the original, notably an ampoule-breaking device (see below), a very small "dead-space" outside the zone of uniform temperature, and an inner tube in which the vapour is released so that there is little danger of vapour penetrating to the cooler parts of the apparatus and condensing there.

FIG. 4.4. Improved Victor Meyer apparatus for vapour density.

A, the vaporization tube, has a bulb about 20 cm long and 5–6 cm wide.

The neck is about 20 mm bore and about 15 cm long, and carries a capillary side-arm which is connected by pressure tubing (wired) to a Hempel gas burette filled with water. If a gas burette is not available a substitute can be constructed readily from an ordinary burette by fitting a rubber stopper with 3-way tap to the top, and connecting a levelling tube by a length of rubber tubing to the bottom. Ideally, the gas burette should be surrounded by a water-jacket. An inner glass tube, B, has a bore of about 15 mm, and is slightly narrowed at the bottom in order to retain a *loose* plug of glass wool C. The upper end of B has the same diameter as the neck

of A, to which it is connected by a piece of wide rubber tubing. The ampoule-breaking device consists of an outer metal tube D (e.g. of copper, about $\frac{1}{2}$ in outer diameter) which fits loosely inside B. D has a slot about $\frac{1}{4}$ in wide and $\frac{1}{2}$ in long cut in its lower end and two metal lugs (d,d) soldered to the upper end. Inside D is a loosely fitting brass rod, E, which contains a $\frac{1}{8}$-in hole through it transversely about $\frac{1}{4}$ in from the bottom. The bottom of E is kept level with the bottom of D by a shoulder, e, which brings its diameter equal to that of D to which it is joined by a nicely fitting sleeve of rubber tubing g. This sleeve is lubricated with grease so that E can be rotated inside D by turning the lugs (f,f) when it is required to break the capillary of the tiny ampoule, F, which contains a weighed amount of the liquid to be vaporized. Ampoules are made from thin-walled glass tubing or, better, from the smallest size of ignition tube by the steps illustrated in Fig. 4.4 (c); a micro-burner or a blow-lamp with a small, pointed flame is needed for this work. Starting from an ignition tube (i), a capillary neck not more than 2 mm in diameter is first pulled out (ii), and a bend is then made near the bulb (iii). At this stage the dimensions should be checked to make sure that the completed ampoule will go inside the tube B. The ampoule is then weighed while at stage (iii), and about 0·1 ml of the liquid which is to be vaporized is introduced into the bulb by the aid of suction, if necessary. The capillary is then sealed off as at (iv), and, when cool, the two glass pieces are weighed together to obtain the weight of liquid in the bulb. The ampoule is suspended with its capillary through the hole in the brass rod E, and ampoule and breaker are carefully lowered into place in the tube B, which is securely closed by the rubber stopper J.

The vaporization tube is heated by boiling a liquid in the jacket G, which is preferably of Pyrex. The boiling point of the liquid should be at least 20–30° above that of the liquid to be vaporized. (See Table A1, p. 351, for suitable heating liquids.) If steam is suitable, the jacket G can have an outlet at the bottom, and steam from a separate boiler can be passed through G. Otherwise a small condenser should be attached to the tube H. A few pieces of porous pot help to prevent "bumping" of the boiling liquid. In order to improve the steadiness of temperature, the tube G may be lagged with asbestos string; another improvement is to use an immersed electrical heating element as recommended for determinations of the boiling point of liquids (Ch. 7, p. 146). The cork stopper, I, must, of course, be cut across to allow the apparatus to be assembled.

Procedure. Having assembled the apparatus and inserted an ampoule containing a known weight of liquid, a test should be made for leaks by introducing a considerable volume of air into the gas

burette and then compressing it into the apparatus by a head of water; if the water level in the burette remains steady after compression, the apparatus is free from leaks.

The liquid in G is now boiled vigorously so that the whole of the tube A is bathed in condensing vapour.   Meanwhile, the three-way stopcock on the gas burette is open to the air so that the pressure inside A remains atmospheric.   After 10 minutes this tap is turned so as to connect A with the burette, the water is levelled, and the volume read every minute until it becomes quite constant, showing that the whole of the vaporization apparatus has taken up a steady temperature.   If the water level in the burette is not close to the top, it should be readjusted by expelling some air from the 3-way tap, followed by levelling again after re-establishing connection with A.

When a quite steady state is reached, the burette reading is noted, and the capillary of the ampoule is broken by rotating the rod E inside the tube F; the lugs d,d, and f,f, are provided to facilitate this operation.   Since the liquid is already at a temperature above its boiling point, vaporization is almost instantaneous, and air is forced over into the burette.   The water level should be lowered to keep the pressure in the apparatus atmospheric, thus minimizing the chance of leakage occurring.   As soon as the volume of air in the burette becomes constant, the water levels are carefully adjusted and the volume of air displaced into the burette is determined.   The temperature of the burette is noted, and the barometer is read.

After each experiment, all vapour must be removed from the tube by suction through a long glass tube which passes to the bottom of the tube B.

Calculation.   Let V be the volume of air displaced into the gas burette; t ($^\circ$ C) the temperature of the burette; b the barometric pressure in mm Hg; f the vapour pressure of water at the temperature t; W the weight in grams of the substance taken; V' the actual volume of vapour produced by vaporization of the substance in the heated part of the Victor Meyer apparatus, at temperature t'.

The vaporization of the substance displaces a volume V' of air from the region of temperature t' to the burette at temperature t, where its volume contracts to V.   If Avogadro's hypothesis were accurately followed, the number of molecules of air displaced would be exactly equal to the number of molecules of the substance vaporized.   The former can be calculated from the pressure and volume of air collected in the burette. Reduced to S.T.P., the quantity of air is $V_0 = \dfrac{V \times 273 \times b}{(t+273) \times 760}$ ml, and since 1 mole would have occupied 22,400 ml, the number of moles of air is $V_0/22,400$.   This is therefore also the number of moles in W g of the substance vaporized, the molecular weight of which must therefore be $22,400 . W/V_0$.

An obvious correction that ought to be applied to the above calcula-
tion is for the pressure of water vapour in the burette. The air is satu-
rated with water, and hence its own pressure is less than atmospheric,
namely $(b-f)$, which ought to be used in place of b in calculating V_0.
However, this correction would be appropriate only if the air displaced
from the bulb were perfectly dry. If the air in the bulb had a relative
humidity (before the tube was heated) of $h\%$, the correct expression in
place of b is $[b(b-f)/(b-fh/100)]$. If the relative humidity of the atmos-
phere is not known, an average value of 50% may be taken for h. A table
of values of the vapour pressure of water at different temperatures is given
in the Appendix (p. 353).

Refinement. The above calculation cannot lead to *accurate* values of
molecular weights from vapour densities since vapours depart appreciably
from the ideal gas laws. However, the true density of the vapour at the
temperature of vaporization, t', can be calculated with little error
(provided t' is known) since the gas concerned (namely, air) exhibits little
departure from the gas laws. Hence $V' = \dfrac{V \times (t' + 273)}{(t + 273)} \times \dfrac{p}{b}$ where p is the
true pressure of air in the gas burette, corrected for humidity as above.
The vapour itself exists, of course, at full barometric pressure b. As the
equation of state of the vapour is unlikely to be known, one may assume
that it would obey the equation of van der Waals, the constants of which
may be calculated from the critical constants of the substance, if known.[3]
(See above, p. 63.)

Analysis of binary mixtures. Vapour density determinations can
be employed to analyze binary mixtures of volatile liquids, provided
the molecular weights of the components differ considerably. If the
pure components give vapours of density d_1 and d_2, and a mixture
containing w_1 g and w_2 g of the two components gives a vapour
density d, then $(w_1 + w_2)/d = w_1/d_1 + w_2/d_2$, or,

$$w_1/w_2(1/d - 1/d_1) = 1/d_2 - 1/d$$

Hence the ratio w_1/w_2 can be calculated.

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CHAPTER 5

THE PROPERTIES OF LIQUIDS

5A. DENSITY

The density or specific gravity of a liquid is the mass of unit volume of the liquid, the unit of volume being the cubic centimetre (cm^3) or the milliletre (ml). The latter unit is now generally adopted. Since, by definition, the millilitre is the volume occupied by 1 gram of water at the temperature of maximum density (4°), the density of water at this temperature, in g/ml, is unity; and the density at any other temperature is expressed relatively to that of water at 4° as standard and represented by $d_{4°}^{t°}$ (weighings are supposed to be corrected for the buoyancy of the air).

The relative density is the ratio of the weight of a given volume of the substance to the weight of an equal volume of water at the same temperature ($d_{t°}^{t°}$); and the density of the substance at temperature $t°$ is equal to the relative density multiplied by the density of water at that temperature.
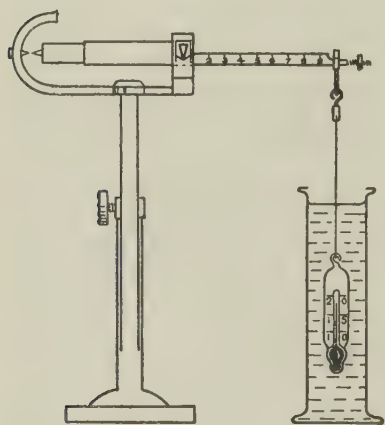

FIG. 5.1. Westphal balance for density of liquids.

Densities of liquids are generally measured either by weighing a definite volume of the liquid in a density bottle or pyknometer or by determining the buoyancy acting on a "sinker" immersed in a liquid (Principle of Archimedes). Small *changes* of density are sometimes determined by measuring the *rate* of rise or fall of a small immersed quartz "float" of pre-arranged overall density.

Where sufficient liquid is available, the density can be determined, approximately, by means of hydrometers, or more accurately, by means of the Westphal balance (Fig. 5.1) which is a simple apparatus for the sinker method. The beam of the balance is graduated into ten equal parts, and four weights, in the form of "riders", are

provided. The masses of these are in the ratios $1 : 0.1 : 0.01 : 0.001$.
In carrying out a determination of the density, the balance is first
adjusted for pure water. The glass sinker, which encloses a thermo-
meter, is suspended in pure water from the end of the balance beam,
and the unit rider is placed on the mark 10, or hung on the hook at
the end of the beam, if only 9 divisions are shown on the beam. By
means of a threaded counterpoise on the end of the beam, or by
means of a levelling screw of the balance, the latter is adjusted till
the two pointers are opposite each other. The depth to which the
sinker is submerged below the surface of the liquid and the tempera-
ture (say $t°$) should be noted.

The sinker is then dried and suspended in the liquid, the density
of which is to be determined, the depth of submersion of the sinker
being approximately the same as before. The temperature of the
liquid should also be the same as that of the water previously used.
If the density is less than unity, the unit rider, which was placed at
the end of the beam in the case of water, must be moved to another
mark on the beam, and other riders must be placed at appropriate
points so as to secure equipoise. If, in order to obtain equilibrium,
the unit rider must be placed on mark 8, the 0.1 rider on mark 7,
and the 0.01 rider on mark 9 and the 0.001 rider on mark 3, the
specific gravity of the liquid is 0.8793. (The riders are bent so as to
form hooks on which other riders may be placed. In this way more
than one rider may be placed at the same mark on the beam). The
value thus obtained represents the relative density, $d_{t°}^{t°}$, of the
liquid.

If the density of the liquid is greater than unity, one of the unit
riders is placed at the mark 10 and the other unit rider and the smaller
riders at appropriate points on the beam. Of course, an ordinary
balance may also be used for the sinker method. An accuracy of
1 in 10^4 is obtainable.

When only small quantities of liquid are available, or where greater
accuracy is required, the density of liquids is best determined by
means of vessels of accurately defined volume, called pyknometers.
These are made in very varying shapes, but the simplest and most
generally useful form is the Ostwald modification of the Sprengel
pyknometer (Fig. 5.2a). The volume of the pyknometer should be
about 5–15 ml. This will allow of an accuracy of about 1 unit in
the fourth place of decimals, which will be quite sufficient for general
purposes.

In carrying out a determination of the density of a liquid, the
pyknometer must first of all be cleaned and dried, by washing well
with distilled water (if necessary, with other solvents first, then with
water), and then, successively, with a small quantity of alcohol

(redistilled methylated spirit) and of ether. A current of clean air is then drawn through the tube.

The pyknometer, cleaned and dried, is first weighed empty. For this purpose it is suspended from the end of the balance beam by means of a double hook (Fig. 5.2 (b)), made of glass, or of platinum or copper wire. (It is not advisable to attach a wire permanently to the pyknometer, because of the greater difficulty in removing all moisture after the pyknometer has been immersed in water.) The pyknometer is then filled with distilled water by attaching a piece of rubber tubing to the end b, and sucking gently while end a dips in the water. The pyknometer is then suspended in a large beaker of water (or, better, a thermostat, Ch. 3) the temperature of which
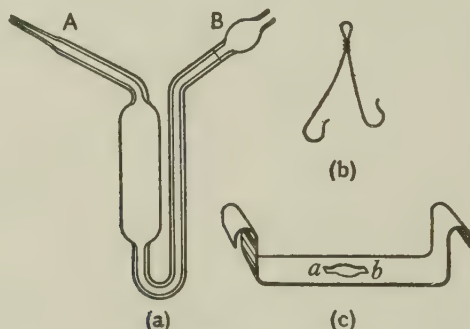

FIG. 5.2. Pyknometer for liquids.

(a) Pyknometer vessel.
(b) Wire support for weighing.
(c) Bracket for supporting pyknometer in thermostat.

must be kept constant to within 0·1°, as shown by a thermometer immersed in the water.

The pyknometer may be suspended in the bath by means of a wire hook placed over a glass rod laid across the top of the beaker; but it is better to use a holder cut from sheet zinc or copper (Fig. 5.2 (c)), and furnished with lugs which can be hooked over the edge of the bath. In the sheet of metal a hole is cut, which allows the body of the pyknometer to pass through, while the arms rest against the ends a and b. The length of the opening should be such as to allow the pyknometer to pass so far through that the mark on the tube b of the pyknometer is just above the metal plate; and the water in the bath should be of such a height that it just touches the underside of the plate. By means of this arrangement, the danger of water getting into the ends of the pyknometer tubes is avoided, and the pyknometer is held in position more securely than by hooks.

When the pyknometer and its contents have taken the temperature

of the bath (say after 15–20 minutes), the amount of water must be adjusted so that it fills the pyknometer from the point of the tube a to mark on b (Fig. 5.2 (a)). If there is too little water, a rod or tube carrying a drop of water is placed against the end of the tube a, when water will be drawn into the pyknometer by capillarity. If there is too much water, a piece of filter paper is carefully placed against the end of a, whereby water can be drawn from the pyknometer until the meniscus stands exactly opposite the mark on b. Instead of using filter paper, the adjustment can be made by gently compressing a short length of rubber tubing attached to the end of b until the meniscus is driven down to the mark. Before releasing the tube any drop of water which may have collected at the point of a is removed by means of a glass rod.

The pyknometer is now removed from the bath, and the outside carefully dried by means of a cloth; care must be taken that none of the water is expelled from the pyknometer by the heat of the hand or by the natural expansion of the liquid when the density is being determined at temperatures below that of the room. When the pyknometer has taken the temperature of the balance case, it is weighed. If concordant and accurate weighings are to be obtained, it is essential that the outside of the pyknometer shall always be dried and treated in exactly the same way, since otherwise the amount of moisture which remains on the surface will vary, and may cause an appreciable error.

When the weight of the pyknometer filled with water has been determined, the pyknometer is emptied and dried and filled with the liquid the density of which is required. It is placed as before in the bath at constant temperature, the liquid is adjusted to the mark, the pyknometer dried with a cloth as before and weighed.

Calculation of the density. If the temperature at which the pyknometer is filled with water and with the other liquid is the same, then the ratio of the weight of liquid (W') to the weight of water (W) gives the approximate density (uncorrected for the buoyancy of the air) of the liquid compared with that of water at the same temperature. This is represented by $d_{t^\circ}^{t^\circ} = W'/W$. For certain purposes, as in the determination of the relative viscosity (Section 5C), this ratio is all that is required; but in all cases where the specific gravity of the liquid is desired, we must compare the weight of the liquid at the temperature t° with the weight of the same volume of water at 4°. The density of the liquid at temperature t° compared with water at 4° is then given by the expression $d_{4^\circ}^{t^\circ} = W'D/W$ where D is the density of water at t°. (See Appendix Table A4.)

The value of the density just given must still be corrected for the buoyancy of the air by taking into account the density of the latter, and one therefore obtains as the expression for the specific gravity of a liquid:

$$d_{4^\circ}^{t^\circ} = W'D/W - 0.0012\,(W' - W)/W$$

If the temperatures at which the pyknometer is filled with water and with the other liquid are not the same, a further correction is necessary for the expansion of the glass, and one obtains as the general expression for the specific gravity of a liquid:

$$d_{4^\circ}^{t^\circ} = \frac{W'D}{W} - \frac{0.0012\,(W'-W)}{W} + \frac{W'D}{W} \times 0.000024\,(t-t')$$

In this expression W is the apparent weight of water in air at temperature t; W' is the apparent weight of the liquid in air at temperature t'; D is the density of water at the temperature t; 0.000024 is the coefficient of cubical expansion of glass; 0.0012 is the mean density of air.

Note: The use of either of the two formulae given above for the calculation of the density may introduce errors in the fifth decimal place of the density value, owing to variations in the value of the density of the air. In the following table are given the values of the density of air half saturated with moisture, at different barometric pressures (corrected):

Temper-ature	Pressure in millimetres				
	740	750	760	770	780
10°	0.001211	0.001228	0.001244	0.001261	0.001278
15°	0.001190	0.001206	0.001222	0.001238	0.001254
20°	0.001168	0.001184	0.001199	0.001215	0.001230
25°	0.001146	0.001162	0.001177	0.001193	0.001208

(For a discussion of various formulae for correcting for the buoyancy of the air, the papers quoted in Bibliography 5A [1] should be consulted.)

EXPERIMENT

Determine the gram molecular volume of pure ethanol at 25.0° C and its partial molal volume in dilute aqueous solution.

Molar, and partial molar volumes can be calculated from accurate density data (see below). The experiment therefore consists in measuring accurately the density of pure ethanol and of a number of ethanol-water mixtures by the pyknometer method as described above. At least four solutions should be made up accurately *by weight* in stoppered flasks—for example, approximately, 5, 10, 15 and 20 weight per cent—and their densities determined. The work can be expedited by using two pyknometers, and, if available, an "aperiodic" balance (Ch. 2).

Calculation. The density of water at 25° C is 0.99707 g per ml. Hence, the density of ethanol and the ethanol-water solutions can be calculated. The specific volume is 1/density (ml per g). The molecular weight of ethanol is 46.07 and hence its molecular volume V_m is 46.07/density (ml per mole).

Partial quantities[2] are important in the theory of solutions; they are introduced because the extensive properties of solutions (e.g. volume, heat capacity, energy, etc.) are not precisely additive when solutions are formed from the pure components. In the present problem, there is a small volume change when alcohol and water are mixed, and consequently when alcohol is added to water or an aqueous solution of ethanol the increase in volume is not exactly at the rate of V_m ml per mole, but at a different rate $\bar{V}$, which depends on the composition of the solution to which the addition is made. *Partial* functions such as $\bar{V}$ can be expressed on any concentration scale, but in thermodynamics *molality* is most convenient—that is moles of solute per 1,000 g of solvent. If the increase of volume of solution containing 1,000 g of water is dV when dm mole of solute is added (dm being too small to affect the concentration, m, appreciably) then $dV/dm = \bar{V}$, the partial molal volume. V can be regarded as the "effective" molar volume of alcohol in the solution. (Similarly, the water has a partial volume $\bar{V}_w$ in the solution.) To calculate $\bar{V}$ for ethanol one can draw a graph of V, the volume of solution containing 1,000 g of water, as a function of m, the molality of alcohol, and the slope (i.e. tangent) gives dV/dm. V and m can be calculated of course from the measured densities and weight concentrations.

Compare V_m and $\bar{V}$; for a hypothetical "ideal" solution these quantities would be equal, as such solutions are formed without change of volume.

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Reilly and Rae, Vol. 1, Ch. 12 (3).
[1] Wade and Merriman, *J. Chem. Soc.*, 1909, **95**, 2174; Archibald and Ure, *ibid.*, 1924, **125**, 728; Barr, *ibid.*, p. 1040.
[2] For further explanation of partial molal quantities a textbook of chemical thermodynamics should be consulted.

5B. VAPOUR PRESSURE OF LIQUIDS

Theory. When a liquid is introduced into an evacuated vessel, some of it evaporates (with absorption of latent heat) until a certain *saturation vapour pressure* is set up which is in equilibrium with the liquid. This pressure, p, has a definite value at a given temperature, T ($^\circ$ K), for a given pure liquid. At equilibrium the rate of evaporation of molecules from the liquid is equal to the rate of condensation of molecules from the vapour into the liquid, and the vapour-liquid equilibrium can be treated either by the kinetic theory or by thermodynamics. The relationship between p and T obtained from either method is

$$\frac{d \log_e p}{dT} = \frac{L}{RT^2}$$

in which L is the molar latent heat at T° and R is the gas constant and equal to 1·99 cal per mole per degree. This equation is a form of

the Clapeyron-Clausius equation and is valid provided the molar volume of the liquid is negligible compared with that of the vapour, and the vapour may be assumed to obey the ideal gas laws. If the further assumption is made that L is a constant for the temperature range T_1 to T_2 the equation can be integrated, and gives

$$\log_e \left(\frac{p_2}{p_1}\right) = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or, in terms of decadic logarithms,

$$\log_{10} \left(\frac{p_2}{p_1}\right) = \frac{L}{2 \cdot 303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This vapour pressure equation holds fairly accurately for liquids (or solids) over a limited range of temperature, and a graph of $\log_{10} p$ against $1/T$ gives a straight line of slope $-\dfrac{L}{2 \cdot 303R}$. This graph, however, shows appreciable curvature if plotted for a wide range of temperature, because L (and hence, the tangent of the line) decreases with rise of temperature, according to the Kirchhoff equation.

The above relationships apply to vapour pressure of all liquids and solids, whether at normal, high or low temperatures, but, naturally, different experimental techniques are needed according to the pressure range concerned. In addition, several distinct methods are in use; four typical ones are described below.

Methods. In *static methods*, the pressure exerted when excess liquid is introduced into an evacuated vessel is measured directly or indirectly. For temperatures below that of the surroundings, the pressure can be measured directly (as in Method 1) on a mercury or other manometer of suitable sensitivity. For higher temperatures it is necessary to interpose a pressure-sensitive glass membrane (e.g. "spoon" gauge, Fig. 5.3) or liquid barrier (as in the isoteniscope, Method 2) between the vapour and the manometer, otherwise liquid distils from the warmer to colder parts of the apparatus. The pressure of air needed to counterbalance the vapour pressure is then measured. In static methods it is essential to remove dissolved air from the liquid (see below).

There are two principal *dynamic methods*. The first is equivalent to determining the boiling point of the liquid at a series of different pressures; clearly a liquid boils when its vapour pressure equals the pressure in the vessel containing it. There are several procedures for measuring boiling points under reduced pressure—for example, the method of Ramsay and Young (Method 3) and various micro methods.[1] The standard method of measuring boiling points accurately (Ch. 6) can readily be adapted to work at different pressures by

means of a manostat or simple pressure-regulating apparatus such as that shown in Figs. 5.5 and 5.7.

The other dynamic method, sometimes called the gas-saturation or transpiration method, consists in passing through the liquid a measured volume of a gas that is chemically inert to it, and determining the quantity of liquid carried away by the saturated gas. This method, being cumulative, is particularly suitable for liquids of rather low vapour pressure. *Very* low vapour pressures such as those given by high-boiling oils, liquid or solid metals, etc., are best measured by one of the *high vacuum methods*—for example, by determining rates of evaporation or effusion, or by the molecular bombardment pressure exerted by the vapour.[1] Methods of determining *partial* vapour pressures, e.g. of solutions, by comparison with solutions of known vapour pressure (the "isopiestic" method) are mentioned in Ch. 6. The vapour pressure over salt hydrates is considered in Ch. 7.

FIG. 5.3. Principle of the glass "spoon" gauge. (*a*, *b* are flexible, being very thin.)

Method 1. The direct, static method (low temperatures). Fig. 5.4 shows a simplified apparatus suitable for measuring vapour pressures in the range 1–100 cm Hg and for temperatures between $-80°$ C and that of the laboratory. The essential parts are the bulb *A* containing the liquid, the manometer *B*, and arrangement *C D E* for removing air from the apparatus. It will be realized that in research practice an all-glass apparatus sealed to a high-vacuum "line" would be used, but the simplified apparatus shown is adequate for volatile liquids such as ethyl ether.

The bulb *A* is almost filled with the liquid and is then connected by a gas-tight joint *c* to the rest of the apparatus. If *c* is of rubber pressure-tubing it should be wired or waxed; alternatively it may be a ground glass joint or glass seal. *A* is cooled in a liquid bath which is preferably contained in a small thermos flask *F*. Temperatures down to $0°$ C may be obtained by adding ice to water. The range $0°$ to $-21°$ C is conveniently covered by a freezing-mixture of ice with various salts (p. 54). If lower temperatures, down to $-78°$ C are required, freezing-mixtures may be prepared with solid carbon dioxide (pp. 54–5). Temperatures should be measured with a low temperature mercury, alcohol or pentane thermometer graduated in degrees or tenths. The thermometer should be checked at two or three known temperatures (Ch. 3).
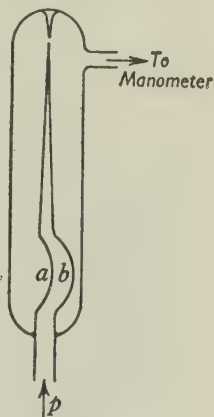
Before the vapour pressure can be measured, all air must be removed from the apparatus. To do this, the pressure is first of all reduced as far as possible by means of a good filter pump, which is connected to the flask E, the 3-way tap C being in position (i); mercury in limb a of the manometer rises to a certain level, but not to the top because the tube is more than 76 cm high. However, the mercury can be made to rise temporarily to C, thus displacing air from this section, by raising the level in limb b. This can be achieved by having limb b attached by a length of rubber tubing so that it can be raised, or by pouring extra mercury into b, in which case an outlet (as at d) must be provided for subsequently lowering
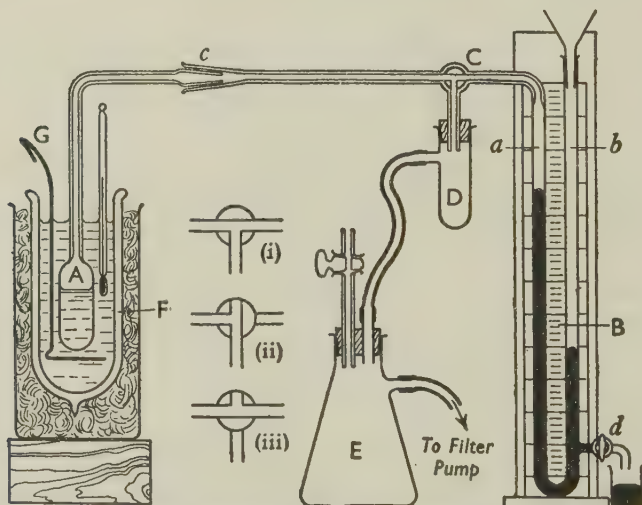
Fig. 5.4. Simple form of apparatus for determination of vapour pressure of liquids by the static method at temperatures below that of the laboratory.

the level, *or* (simplest of all) by pushing a loose-fitting glass rod down into limb b. A little mercury is driven over into D and the tap C is immediately turned into position (ii). When the mercury level in b is lowered again, a fairly good vacuum is obtained above the mercury in limb a. Meanwhile the liquid in A is subjected to the lowest pressure obtainable with the filter pump, the 3-way tap being in position (ii). Some of the liquid evaporates and the vapour sweeps air from the apparatus between A and C. Finally the tap C is turned smartly into position (iii), thus admitting vapour to the manometer and isolating the pump. If air has been removed successfully the pressure inside the apparatus will be the vapour pressure of the liquid at the temperature of A, and the manometer B will register

the difference between p and the atmospheric pressure, B, which must be read on a barometer.   Before proceeding with measurements of vapour pressure with different temperatures in F, it is advisable to check for leaks by putting bulb A into the lowest stable temperature bath available (e.g. ice or solid carbon dioxide).   When the liquid has taken the temperature the manometer levels should remain steady.   It is also advisable to repeat the evacuation process once or twice to ascertain whether air has been thoroughly removed. When the above tests indicate that satisfactory readings are being obtained, a series of determinations can be made at different temperatures without further evacuation.
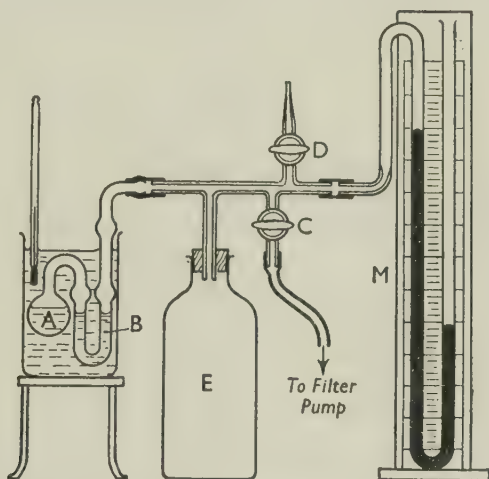
FIG. 5.5. Apparatus for determination of vapour
pressure by the isoteniscope method.

Method 2. The isoteniscope of Smith and Menzies.[2]   The isoteniscope (Fig. 5. 5) consists of a glass bulb A of about 2 cm diameter connected to a small U-tube B with limbs about 3–4 cm long.   The principle of the device is that the pressure of the vapour in A is balanced by an adjustable pressure of air in the external apparatus so that the liquid stands at the same level in the limbs of the U-tube B. The pressure registered by the manometer M is then equal to the barometric pressure *minus* the vapour pressure.   The temperature of A is that of the bath in which it is immersed; this is preferably a small glass-sided thermostat with control gear of a type providing rapid adjustment of temperature.   (Ch. 3B.)

The air pressure is regulated by tap C, which connects to a

filter-pump, and tap *D* which admits air through a capillary leak.
(Alternatively small "doses" of air may be admitted by having two
taps with a small volume between them.)   The large bottle *E* acts as a
buffer to stabilize the pressure; it should be covered by felt and wire
gauze to minimize temperature fluctuations and to guard against
flying glass in case it collapses under vacuum.

To make a determination the apparatus is first assembled and
tested for leaks.   Liquid is then introduced until *A* and *B* are about
two-thirds full.   The pressure is reduced to make the liquid in *A* boil
so that air is displaced from the isoteniscope.   The pressure is then
cautiously restored by opening *D* until the liquid in *B* stands level,
and this balance is maintained while the isoteniscope attains the tem-
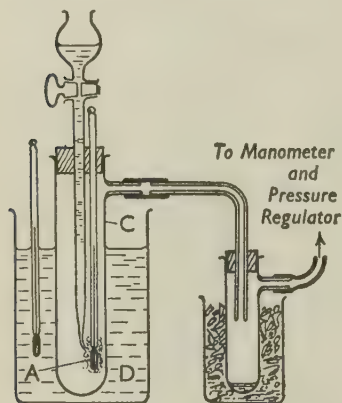perature of the thermostat.   The
final adjustment of pressure is
carried out carefully to bring the
columns of liquid in *B* to the same
level as closely as can be judged by
the eye.   The thermometer, mano-
meter and barometer are then
read.   The evacuation process
and vapour pressure measurement
should be repeated to ensure that
air has been entirely removed.   If
the result is duplicated, further
measurements at other tempera-
tures can be proceeded with, care
being taken that no air gets back
into *A*.   Sufficient time must be
given at each temperature to allow
the liquid to take the temperature

FIG. 5.6. Apparatus for determina-
tion of vapour pressure by the
method of Ramsay and Young.

of the bath; the vapour pressure should then remain steady in-
definitely.

The isoteniscope is particularly suitable for the temperature range
20°–150° C and for vapour pressures of 10 cm to 1 atm.

Method 3. The method of Ramsay and Young.[3]   This is an
ingenious method of obtaining accurate boiling points of a liquid
under reduced pressure.   Super-heating is avoided, and compara-
tively little liquid is needed.   Fig. 5.6 shows a convenient apparatus.

The bulb of a thermometer, *A*, is *thinly* covered with a cotton-wool
wick which is kept moist with the liquid to be studied, the tap-funnel
being adjusted to give a very slow flow of liquid sufficient merely to
replace that evaporated.   The film of liquid around *A* is heated
only by radiation from the outer tube which is immersed in liquid
bath *D*.   The temperature of *D* is maintained at about 10–20° C

above that indicated by *A*. *D* need not therefore be accurately thermostated, but may consist simply of a large beaker of water or oil heated by a Bunsen burner.

A low pressure is maintained in vessel *C* either by an arrangement similar to that used with the isoteniscope and shown in Fig. 5.5 or by some form of automatic pressure regulator ("manostat") of which many forms have been devised.[4]

Manostat. Fig. 5.7 (a) shows a simple reduced-pressure manostat suitable for the pressure range 1 cm Hg to 1 atm. The key component is a sintered glass filter (*A*) of porosity No. 4 — a size which will permit passage of air but not of mercury, even under vacuum. The tube *C* is kept at low pressure by means of a filter pump or oil pump, and the rate of evacuation is adjusted by tap *D* so that it slightly exceeds the rate of leak-
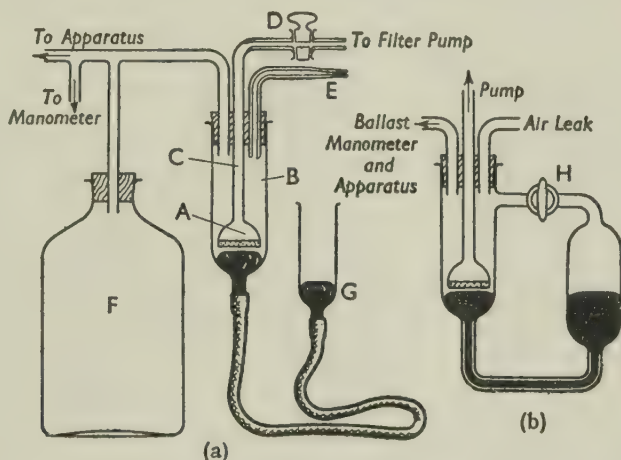

Fig. 5.7. Manostat employing sintered-glass disc and mercury cut-off.

age of air into *B* through a capillary leak *E*. (Easier control is obtained with needle valves at *D* and *E*.) The mercury level rises until it reaches the sintered disc and cuts off the pump. It is important to have a ballast volume *F* connected to *B* to minimize fluctuations. If the disc *A* is exactly horizontal the manostat will work with an on-off action and an oscillation of pressure, but if the disc is slightly tilted a gradual cut-off is obtained, and a pressure steady to better than 0·1 mm can be obtained. The operating pressure of the manostat is readily altered by raising or lowering the reservoir *G*. The manostat can be made much more compact and the inconvenience of a movable mercury reservoir can be avoided by the modified form of apparatus shown in Fig. 5.7 (b). The vacuum stopcock *H* is kept open at first until the pressure, as indicated by the manometer, is reduced to the required value. *H* is then closed, and any further fall of pressure now causes the manostat to operate.

P.P.C.—6

(Incidentally, the same manostat could be used to maintain constant positive pressures somewhat above atmospheric pressure by feeding a slow stream of compressed air in through the tube D and allowing the excess to escape to the atmosphere through the sintered disc A.)

Another convenient form of manostat employs a "Cartesian diver" as the pressure-sensitive element.[4]

In making a measurement by the method of Ramsay and Young, the pressure is first reduced to about 30 mm. Evaporation occurs from the liquid surrounding the thermometer bulb, and the temperature falls. Providing the bath temperature is kept within the limits stated, a steady distillation can be achieved, the rate of supply of heat by radiation being balanced by the rate of cooling by evaporation, and a steady temperature is registered by the thermometer. This temperature and also the manometer reading are recorded. At this temperature the liquid has a vapour pressure equal to the controlled pressure in the apparatus, since the liquid is surrounded by and is in equilibrium with a film of air-free vapour in the interstices of the cotton-wool. Further readings are taken with higher pressures and temperatures until a vapour pressure of 1 atmosphere is reached. If the thermometer thread is entirely in the heated zone no emergent stem correction is needed, but a correction for the effect of reduced pressure—probably 0.1 to $0.2°$ at the lowest pressures—may be found necessary. This correction is determined, of course, with no liquid on the wick, and may be assumed proportional to pressure change and independent of temperature, except for high temperatures.
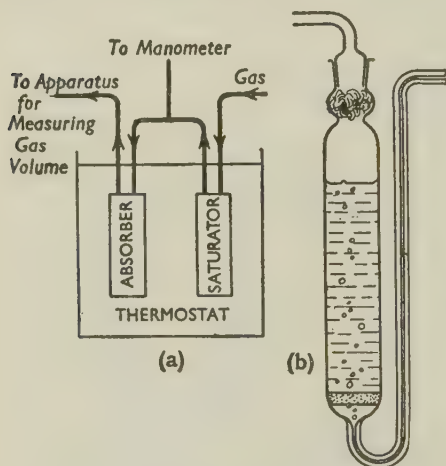

Fig. 5.8. Determination of vapour pressure by the transpiration method.

(a) Arrangement of apparatus (schematic).
(b) Vessel for saturating a gas with a liquid.

Method 4. The transpiration (gas-saturation) method. The essential measurements in this method are (a) the quantity of gas passed, (b) the quantity of liquid (or solid) evaporated, (c) the temperature, and (d) the pressure at the saturator. The general arrangement of apparatus is shown schematically in Fig. 5.8 (a).

There are so many ways in which (a) and (b) may be determined, depending on the substance to be studied, that only general methods will be indicated here.

If the vapour pressure is very low, a large volume of gas will be needed to transport measurable quantities of vapour. Volumes of say 5 litres or more are best measured by a laboratory gas-meter.

Wet gas meters. The pressure of gas in the meter (P_m mm) and also the temperature (t_m) must be determined. The saturation water-vapour pressure at t_m is read off from tables (Appendix p. 353,
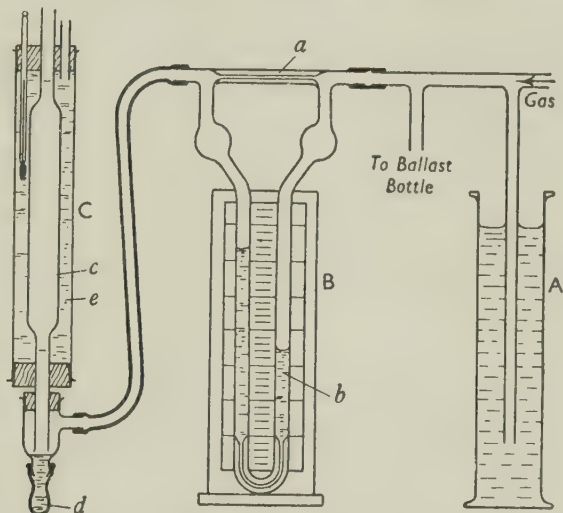

Fig. 5.9. Determination of the rate of flow of a gas by means of a capillary flow-meter (B) or soap-bubble flow-meter (C).

Table A5)—say p_w (mm). Then if V_m (litres) is the volume of (wet) gas indicated by the meter, the content of dry gas is equivalent to $V_m \times \dfrac{(P_m - p_w)}{P_m}$ litres at t_m; or a volume of

$$V_0 = V_m \frac{(P_m - p_w)}{P_m} \times \frac{273 \cdot 1}{(273 \cdot 1 + t_m)} \times \frac{(P_m - p_w)}{760}$$

litres at S.T.P. Wet gas meters must be carefully levelled and filled to the correct level with water before use. They may be tested against a calibrated aspirator bottle.

Gas flow meters. Another method of measuring the volume of gas passed through the system is to arrange a constant rate of flow of gas by means of a manostat (p. 81) or a constant pressure head with "blow-off" (Fig. 5.9, A) and to determine the time of flow

and the *rate* of flow of gas. The latter can be measured by a capillary flow-meter B, or soap-bubble flow-meter C.

Capillary flow-meters are particularly suitable for indicating moderate rates of gas flow; the fall of pressure across the ends of a capillary resistance a, is indicated on a U-tube manometer b, containing for instance, butyl phthalate (density c. 1·05). Since they depend on the viscosity of the gas, capillary flow-meters need calibration with each gas used. Fig. 5.9 shows a suitable method of calibration, using a soap-bubble flow-meter as standard. This device consists of a vertical tube c, which may be a graduated burette or simply a calibrated volume defined by marks at top and bottom. The lower end of c stands a little above a small reservoir of soap solution, the level of which can be made to rise and touch the tube c momentarily when required by compressing the small rubber bulb d. If gas is passed steadily through c, it carries a horizontal soap film upwards, and if the time taken for the film to travel between the two marks is noted, the rate of gas flow can be calculated. The tube c should be surrounded by a water-jacket e to define its temperature. The gas is presumed to be saturated with water vapour, and the volume is therefore corrected as above. Such flow-meters can be made with capacities ranging from 1 ml to 100 ml.

If a sensitive method is available for determining the quantity of liquid transported in the gas-saturation method, it may suffice to pass only a few litres of gas, and this quantity can be most easily measured by running water from an aspirator bottle, measuring it subsequently by volume or weight. The usual temperature, pressure and humidity corrections are needed. Still another method of measuring the gas volume is to employ the vapour pressure method in reverse, i.e. to pass gas through a saturator containing a liquid of accurately known vapour pressure, e.g. water at 0° C, and measure the quantity of vapour transported from it.

Saturators. If a gas is bubbled through a liquid by a simple immersed jet bubbler, it is unlikely to reach saturation at once, and several such bubblers must be used in series. Much better contact between gas and liquid is achieved if the gas has to pass up a column of glass beads or short pieces of glass tubing wet with the liquid. Alternatively the gas stream may be broken into very small bubbles by means of a sintered glass disc, as in the saturator shown in Fig. 5.8 (b). The small bulb above the liquid is packed with glass wool to trap spray which otherwise is easily carried away in the gas stream.

The quantity of liquid evaporated during the experiment can be measured in several ways, namely (i) by loss of weight of the satura-

tor, or (ii) by absorbing or condensing the vapour in another vessel and determining the increase of weight of the absorber, or (iii) by absorbing the vapour and determining the quantity by chemical or physical methods of analysis.

Calculation. The ideal gas laws and Dalton's Law are assumed to hold. The measurements of gas flow lead to a value for V_0, the S.T.P. volume of dry gas passed through the saturator (see above). Since 1 mole of gas at S.T.P. occupies 22·414 litres, the number of moles of carrier gas is $V_0/22·414$. Similarly, the number of moles of liquid vaporized is the mass, w g, divided by the molecular weight of the substance, M. The gas-vapour mixture emerges from the saturator at a total pressure P_s, the vapour being at its saturation vapour pressure p_s and the carrier gas making up the balance, i.e. $(P_s - p_s)$. Since gas and vapour occupy the same volume, namely, the volume of mixture passing out of the saturator, their partial pressures in the mixture must be in the ratio of the number of moles of each, hence

$$\frac{p_s}{(P_s - p_s)} = \frac{w/M}{V_0/22·414}$$

In this equation P_s, w, and V_0 are determined, M is known and therefore the vapour pressure, p_s, can be calculated.

EXPERIMENTS

Determine the vapour pressure of a pure liquid over a range of temperature by one or more of the methods described.

If time permits the use of more than one method, the same liquid can be studied by two methods over a very wide range of temperature. For example, volatile liquids such as ethyl ether, ethyl bromide, or methyl formate may be studied by method 1 for temperatures below room temperature and methods 2 or 3 from room temperature to their boiling points.   Less volatile liquids (e.g. carbon tetrachloride, water, glacial acetic acid, toluene, xylene, pyridine, chlorobenzene, n-heptane, n-octane) may be studied by a combination of method 3 (or 2) (for high pressures) with method 4 for low vapour pressures.

Treatment of results. Plot a graph of $\log_{10}$ (vapour pressure) against $1/T$ ($^\circ$ K), and from the slope of the line calculate the latent heat of vaporization, L_v.   If the accuracy of the results justifies it, the change of L_v with temperature may be obtained.   The results for vapour pressure and for L_v should be compared with published data,[5] and the probable errors in the results should also be estimated.

More reliable values for the latent heats and also better interpolation of the values may be obtained by *comparing* the vapour pressure data for the liquid with those of a similar substance for which accurate vapour pressure and latent heat values have been published.   This depends on the fact that vapour pressure-temperature curves have much the same form for all substances, and deviations from the simple vapour pressure equation therefore tend to cancel in a comparison method.   For example, for

liquid A, the graph of $\log_{10} p_A$ against $1/T$ is slightly curved, being concave to the $1/T$ axis; similarly, for liquid B, $\log_{10} p_B$ shows a very similar degree of curvature. Consequently, a graph of $\log_{10} p_A$ against $\log_{10} p_B$ (at the same series of temperatures) is a straight line over a wide range of temperature. The *exact* Clapeyron-Clausius equation is

$$dp/dT = L/T\Delta V$$

where $\Delta V = (V_v - V_L)$, V_v is the molar volume of vapour (at pressure p), and V_L is the molar volume of liquid. If, instead of assuming that V_v obeys the ideal gas law, one puts $\Delta V = (RT/p) \times \Delta x$, where Δx is a correction factor which allows for non-ideality of the vapour and the small correction for V_L, then

$$\frac{dp}{dT} = \frac{Lp}{RT^2\Delta x} \quad \text{or} \quad \frac{d\log_e p}{d(1/T)} = -\frac{L}{R\Delta x}$$

It is only necessary to assume now that for two similar liquids A and B the correction factor Δx is the same (which is a much closer approximation than taking a factor of unity), and the equation of the comparison graph is obtained as

$$\frac{d(\log_e P_A)}{d(1/T)} = \frac{L_A}{L_B} \cdot \frac{d(\log_e p_B)}{d(1/T)}. \quad \text{Hence} \quad \frac{d(\log_{10} p_A)}{d(\log_{10} p_B)} = \frac{L_A}{L_B}$$

The graph of $\log_{10} p_A$ against $\log_{10} p_B$ therefore has a slope of L_A/L_B and one latent heat can be obtained from it accurately if the other is known. Although both L_A and L_B decrease slightly with rise of temperature, the ratio L_A/L_B is practically independent of temperature and the above graph is therefore a good straight line.

Other, more complicated, methods of treating vapour pressure data have been developed, but most of them use empirical equations.[6]

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[1] See Partington, *loc. cit.*, for further details and references.
[2] Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412.
[3] Ramsay and Young, *J. Chem. Soc.*, 1885, **47**, 42.
[4] Thomson in Weissberger, *op. cit.*; Partington, *op. cit.*, Vol. 1, Sec. 7 (A), 8.
[5] International Critical Tables; Landolt-Bornstein Tables: Stull, *Ind. Eng. Chem.*, 1947, **39**, 517.
[6] Thomson, *Chem. Rev.*, 1946, **38**, 1; cf. Weissberger, *op. cit.*

5C. VISCOSITY

Theory. When a liquid flows through a tube, the layer of liquid in contact with the wall of the tube is stationary whereas the liquid in the centre has the highest velocity; intermediate layers move with a gradation of velocities. The flowing liquid may therefore be regarded as composed of a number of concentric tubes sliding past one another like the tubes of a telescope. Each layer exerts a drag

on the next, and work must be done to maintain the flow. Newton deduced that the internal friction or *viscosity* would produce retarding forces proportional to the *velocity gradient* (dV/dx) (normal to the direction of flow) and to the area of contact (A) between the moving sheets of liquid, i.e. $F \propto A\,dV/dx$, or $F = \eta A\,dV/dx$, where η is a constant. This law holds for all homogeneous liquids, but not for suspensions or colloidal solutions, which are therefore called non-Newtonian fluids (Ch. 14). The proportionality constant, η, is the *coefficient of viscosity*; in c.g.s. units it has the dimensions of g cm^{-1} sec^{-1} and the unit is the *poise*. Common liquids range in viscosity from 0·002 poise (ether) to 8 poise (glycerol), water being about 1 centipoise (10^{-2} poise). Other quantities sometimes employed are the *fluidity*, ϕ, defined as the reciprocal of viscosity, i.e. $\phi = 1/\eta$, and the *kinematic viscosity*, ν, defined as viscosity divided by density, i.e. $\nu = \eta/\rho$.

Kinematic viscosity is more significant than absolute viscosity in problems of hydrodynamics because the flow properties of a liquid depend on inertia as well as internal friction.

Viscosity *decreases* considerably with rise of temperature (roughly about 2% per degree), and follows fairly closely the Andrade equation: namely,

$$\eta = Ae^{B/RT}$$

in which A and B are constants for a given liquid. By analogy with the Arrhenius theory of reaction velocities, (cf. Ch. 13), B, which has the dimensions of work, can be regarded as the "activation energy for viscous flow", although the structural interpretation of the quantity is not quite clear. It is probably related to the work needed to form "holes" in the liquid into which molecules can move, thus permitting relative motion to take place.[1] Viscosity depends on molecular size and, particularly, *length* and also on the magnitude of the intermolecular forces; non-polar organic liquids (e.g. benzene) generally have low viscosities, whereas liquids in which directed bonding can occur between the molecules (e.g. hydrogen bonds in glycerol) have relatively high viscosities. The viscosity of colloidal solutions is discussed in Ch. 14 (pp. 345-8).

Methods of measuring viscosity. Because of the importance of viscosity in many sciences and in technology, numerous instruments for measuring it (*viscometers*) have been developed to suit different needs. A viscometer must provide means of measuring the rate of flow in the liquid and the force exerted or work done in producing the flow. The fundamental equation (above) is applied directly in *rotating cylinder viscometers*. In these a thin film of liquid is sheared between inner and outer concentric cylinders. In the

Couette viscometer the outer cylinder is rotated at constant speed and the force exerted on the inner cylinder is determined by the steady deflection of the torsion wire on which the inner cylinder is suspended.

All other methods depend on flow relationships derived from the fundamental equation. Thus, many forms of apparatus employ flow through *capillary tubes*, and then rely on Poiseuille's equation for such flow, namely:

$$V = \frac{p\pi r^4 t}{8\eta l}$$

V = volume of fluid (viscosity η) passing through a tube of length l, radius r, in time t, when a pressure difference p is maintained between the ends of the tube. This equation holds accurately for "streamline flow", but not for the "turbulent flow" which sets in at high velocities (namely, when the mean velocity of flow along the tube exceeds $1,000\eta/r\rho$ cm per sec). A small error arises in practice because the liquid emerging from a capillary tube possesses appreciable kinetic energy, and since this is not allowed for in Poiseuille's equation a kinetic energy correction is needed. Consequently, accurate *absolute* measurement of viscosity is difficult. As often happens, however, in physical chemistry comparative measurements are entirely satisfactory and much more convenient. In fact, simple U-tube capillary viscometers such as Ostwald's viscometer (see below) are used more than any other type.

Another well-established accurate hydrodynamic law is Stokes's law for the terminal rate of fall (v) of a sphere (radius r, density ρ_1) through a liquid (density ρ_2), namely,

$$v = \frac{2}{9} \cdot \frac{(\rho_1 - \rho_2) r^2 \mathbf{g}}{\eta}$$

In the *falling-sphere viscometer* a ball-bearing is timed in falling a measured distance through a cylindrical tube of liquid. Corrections are needed, however, for the influence of the walls and bottom of the tube. The former is usually quite important; it can be allowed for approximately by introducing a factor of $(1 + 2 \cdot 1 r/R)$ below the line of the r.h.s. of Stokes's law (R = radius of tube).[2] Here again relative determinations with the same tube and ball largely eliminate these complications. The method is particularly suitable for viscous oils which are available in quantity. The simple apparatus of Gibson and Jacobs [3],[7] (Fig. 5.10), is suitable.

Other methods of measuring viscosity depend on more complicated systems of flow—for example, the damping of torsional oscillations of a disc suspended in the liquid on a torsion wire [4] or of a hollow sphere [5] or hollow cylinder [6] containing the liquid.

These methods have been used for liquid metals at high tempera-
tures.   In addition, many technical viscometers are in use for com-
paring empirically the flow characteristics ("rheological properties")
of materials such as oils, paints, clays, etc.

The Ostwald viscometer.   The usual form of this simple, yet
accurate, apparatus for comparing viscosities of different liquids is
shown in Fig. 5.11 (a).   The left-hand limb of the U-tube is essen-
tially a pipette with two defining marks A and B, and a capillary
resistance C through which the liquid contained in bulb D flows
under gravity back into the bulb E in the right-hand limb.   A
definite volume of liquid is employed, and is delivered into tube F
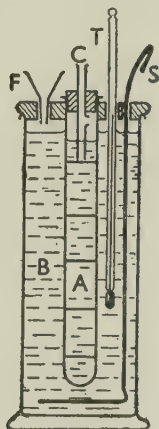

Fig. 5.10. Apparatus of
Gibson   and   Jacobs
for determination of
viscosity   of   a   liquid
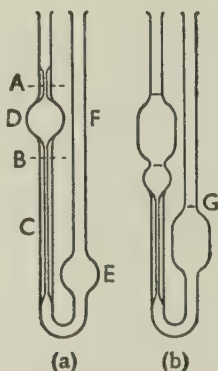by the   falling-sphere
method.[3,7]

Fig. 5.11. Ostwald visco-
meters.
(a) Traditional form.
(b) British Standards In-
stitution form.[7]

from a calibrated pipette; the quantity should be such that when the
liquid is sucked up into the left-hand limb until the meniscus stands
above the mark A then the meniscus on the right stands at the
bottom of bulb E.   The liquid is released from this position and
allowed to flow back.   When the meniscus passes mark A a stop-
watch is started and when it reaches mark B the watch is stopped, and
the time of outflow is noted.

The force driving the liquid through the capillary is equal to
$h \times \rho_1 \times g$, where h is the mean difference of level of liquid in the
two limbs of the tube, ρ_1 is the density of the liquid and g the
gravitational constant.   The resistance to flow depends on the
dimensions of the capillary (which are constant) and on the viscosity

of the liquid. If now, the *same volume* of a second liquid is introduced into the tube, the mean difference of level of the two liquid surfaces will also be h, so that the driving force is now $h \times \rho_2 \times g$. Thus, the driving force is proportional to the densities of the liquids while the resistance is proportional to their viscosities. Since the *rate* of flow is proportional to force/resistance, the *times* of outflow (t_1 and t_2) for the same volume of the two liquids are in the inverse ratio, i.e.

$$\frac{t_1}{t_2} = \frac{\eta_1/\rho_1}{\eta_2/\rho_2}, \text{ or } \frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}.$$

This expression gives the relative viscosities of the liquids; if the absolute viscosity of one of them is known, that of the other can be calculated.

Since the rate of flow through a capillary tube depends on r^4, and r (the internal radius) can be varied from, say, 0·2 mm to 2 mm, Ostwald viscometers can be made to cover a range of 10^4 in viscosity. Suitable dimensions for a set of five viscometers of the "standard" pattern shown in Fig. 5.11 (b) have been recommended by the British Standards Institution.[7]   The No. 0 and No. 1 sizes, which together will suit most ordinary liquids, have capillaries 12 cm long and 0·038 and 0·060 cm internal diameter respectively.

EXPERIMENT

Determine the absolute viscosity of a pure liquid (such as benzene), and the influence of temperature on its viscosity.

Practical details. A viscometer should be selected having a flow time between 1 and 10 minutes with the given liquid. It must first be thoroughly cleaned with warm chromic acid so that there are no obstructions in the capillary and the liquid runs cleanly without leaving drops behind. It is then thoroughly washed by drawing distilled water through it with the aid of a filter pump, and then rinsed with alcohol and ether and dried with a stream of air *filtered through cotton-wool* to exclude dust.

The viscometer is fastened, accurately vertical, in a glass-sided thermostat (or, for temperatures near that of the laboratory, in a large beaker of water). The temperature should be controlled within 0·1°. The mark A should be well below the surface. A piece of rubber tubing, cleaned internally to remove dust, may be attached to the tube above A and used when sucking up the liquid into the left-hand limb. A suitable quantity of liquid, usually about 10 ml, is measured exactly into the viscometer with a pipette, and allowed 10–15 minutes to reach the temperature of the thermostat. The liquid is then sucked up and released, and the time of outflow

between the marks is determined with a stop-watch reading to 0·2 seconds. The determination is repeated a number of times. If the time of outflow is about 100 seconds, the different readings should not deviate from the mean by more than 0·1–0·3 second. Greater deviations point to dust in the capillary tube. To determine the influence of temperature on the viscosity, the time of outflow should be measured at intervals of 5° between, say, 25° and 50°. A small error arises from the change of volume of the liquid owing to expansion, but this may be neglected provided that during the outflow period the lower meniscus lies inside the bulb E, so that the change of level is small. (In the "standard" viscometer, Fig. 5.11 (b), a mark G is provided for adjustment of the level to allow for expansion and also change of surface tension.) The density of the liquid at each temperature will be required; this may be determined by means of a pyknometer or Westphal balance (p. 70) or taken from standard tables. The viscometer must be calibrated separately at one temperature with exactly the same volume of a liquid of known viscosity and density, usually water, the viscosity of which may be taken as 0·895 centipoise at 25·0° C. Pure aniline ($\eta_{25} = 3·61$ cP, $\rho_{25} = 1·017$) could be used for calibrating No. 1 size viscometers, and 60% (by wt.) sucrose solution ($\eta_{25} = 43·5$ cP, $\rho_{25} = 1·28$) for higher range viscometers.[8] Special oils can also be obtained for calibrating viscometers.

Treatment of results. From the densities and times of flow calculate the absolute viscosity of the liquid at each temperature. By plotting the fluidities ($= 1/\eta$) against the temperature, a graph of gentle curvature is obtained, which is convenient for interpolation of values. Compare the results with published data. Plot also $\log_{10} \eta$ against $1/T(°$ K); a straight line graph should be obtained if Andrade's equation is followed, and the slope is equal to $E/2·303R$ (see p. 87). It is instructive to plot also a graph of fluidity against specific volume ($= 1/\rho$) of the liquid at each temperature. The approximate straight line which results suggests a close connection between the ease of flow and the "free volume" in the interstices of the liquid.

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[2] For further details see Merrington, *op. cit.*
[3] Gibson and Jacobs, *J. Chem. Soc.*, 1920, **117**, 473.
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[6] Hopkins and Toye, *Proc. Phys. Soc.*, 1950, **63** (B), 773.

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[8] See Int. Crit. Tables, Vol. 5, p. 23.

5D. SURFACE TENSION

Theory. Surface tension is a manifestation of the forces of attraction that hold the molecules together in the liquid (or solid) state; thus, liquid droplets tend to become spheres—the form of least surface area—because of the mutual cohesion of the molecules. Conversely, work must be expended to increase the surface area of a liquid, as in expanding a soap bubble. The reality of surface tension (γ) is convincingly demonstrated in the Dupré frame experi-
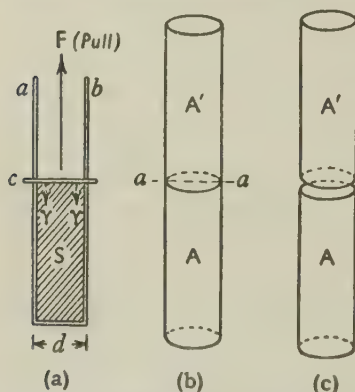

FIG. 5.12. Significance of surface tension.

(a) Dupre frame experiment—force exerted by a soap film.
(b), (c) Relation of surface energy to cohesion (see text).

ment (Fig. 5.12 (a)) in which a smooth wire c slides on two parallel wires a and b and stretches a soap film S. If a force F dynes, is needed to balance the pull of the film (width d cm), then $F = 2d\gamma$, since γ is the force per unit length of the surface, and in this experiment there are two surfaces of liquid. If c is advanced by 1 cm, the work done is $F \times 1$ ergs, while the surface area increases by $2 \times d \times 1$ sq. cm. Therefore, the work required to form 1 sq. cm of new surface is $F/2d = 2d\gamma/2d = \gamma$ ergs. This shows that γ can be regarded either as a *tension* (dynes per cm) acting along the surface or as surface (free) *energy* (in ergs per sq. cm), the two concepts being entirely equivalent. The relation between surface energy and intermolecular forces can be readily appreciated by an imaginary experiment illustrated in Fig. 5.12 (b) and (c). Imagine a column of liquid AA' to be torn apart across the plane aa (area 1 cm^2). Work is required to separate the two parts against the cohesive forces ("work of cohesion"); this work is equal to twice the surface energy since two sq. cm of new surface are thus formed. It is understandable, therefore, that high surface tensions are found with liquids which have strong cohesive forces and consequently high latent heats of vaporization and high boiling points (e.g. liquid metals), whereas volatile organic liquids (e.g. ether) have low surface tensions. Similarly, for a given liquid,

the surface tension, like the latent heat, decreases with rise of temperature and becomes zero at the critical point.

At temperatures not too close to the critical temperature, γ decreases linearly with temperature, but a relationship more accurate for a wide range of temperature is that discovered by MacLeod (1923), namely, $\gamma = k(\rho_l - \rho_v)^4$, where ρ_l and ρ_v are the densities of the liquid and the vapour and k is a constant. (ρ_v is generally negligible compared with ρ_l.) Sugden (1924) found that the k values of different substances can be correlated by use of a function called the *parachor*, which is defined by $[P] = M\gamma^{\frac{1}{4}}/\rho_l$. ($M = $ mol. wt.) The parachor is an additive property so that the value for a given molecule can be calculated as the sum of a series of atomic and structural constants, of which the following are a few values.

ATOMIC AND STRUCTURAL PARACHORS

C	4·8	Double bond	23·2
H	17·1	Co-ordinate linkage	−1·6
N	12·5	Triple bond	46·6
O	20·0	3-membered ring	16·7
O_2 in esters	60·0	4-membered ring	11·6
P	37·7	5-membered ring	8·5
S	48·2	6-membered ring	6·1
Cl	54·3	Singlet linkage	−11·6

The parachor is not entirely without constitutive influence; it is therefore, unfortunately, not as reliable a guide to molecular structure as was originally thought. It is useful, however, for estimating values of surface tension of liquids of known structure and density.

If the imaginary experiment of Fig. 5.12 (b, c) were conducted with columns A and A' of *different*, immiscible, liquids, the work required would give information about the *work of adhesion* of the liquids. Clearly, an interface between any two phases has surface energy (*interfacial energy*) analogous to that of a liquid–gas surface, and the corresponding force required to extend the interface is called the *interfacial tension*. This quantity is of interest in connection with wetting phenomena, detergency and emulsification (Ch. 14). The relation between surface (or interfacial) tension and adsorption is considered in Ch. 14.

Methods of measuring surface tension. The innumerable methods that have been described can be classified into six groups: (1) direct measurement of capillary pull (Wilhelmy, du Nouy), (2) capillary rise (in single tubes, differential tubes, parallel or inclined plates), (3) bubble pressure (Jaeger, Sugden, Ferguson), (4) size of drops (weight or volume), (5) shape of drops or bubbles, (6) dynamic

methods (ripples, etc.).   In almost every case the elementary theory of the method needs correction if accurate results are required. The choice of a method will depend on whether the primary consideration is extreme absolute accuracy, practical convenience, speed of working, small size of sample, or study of time effects.   The capillary rise method is the most accurate absolute method, but results accurate to better than 0.5% can be obtained much more conveniently by the drop weight, ring detachment, or bubble pressure methods.   As elsewhere in physical chemistry, it is rarely necessary to use a laborious absolute method since most of the difficulties can be circumvented by calibrating the apparatus with a liquid of known surface tension.   Some other difficulties can be avoided by employing a *differential* method (see Methods A and B below).

Scrupulous cleanliness is essential in surface tension work; aqueous solutions, in particular, are highly susceptible to contamination by minute traces of grease, with large reduction in their surface tension.   Consequently, from this point of view, the methods in which fresh drops or bubbles are repeatedly formed offer an advantage over static methods such as capillary rise.   For the same reason a form of apparatus that can be readily cleaned and protected from contamination is desirable and, in addition, it should be suited to immersion in a thermostat to control the temperature within $0.1°$. Four convenient methods are described in this section, and some other methods particularly suitable for the study of surface films and small changes in surface tension are given in Ch. 14.

A. Capillary rise. (*Differential form with calibration*).   The elementary technique and theory are well known but inaccurate. With proper corrections and experimental procedure high accuracy (better than 0.05%) has been achieved,[1] but the method is then slow and difficult.   A modification which is much simpler and yet capable of yielding results accurate to 0.1% is described below.   The chief difficulties met with in the absolute method are as follows: (i) the difficulty of selecting and measuring accurately the bore of a capillary tube of uniform bore: this is overcome in the present modification by calibrating the tube with water or benzene, the surface tensions of which have been accurately established, and by working always with the meniscus at one position in the tube; (ii) the necessity for having a very wide surface of liquid (> 4 cm) for the lower level if it is to be assumed plane, and the consequent need for much liquid; (iii) the associated experimental difficulty of accurately measuring the level of a wide surface of liquid: these last two difficulties are avoided by using two capillary tubes of different bore.

A differential capillary rise apparatus is shown in Fig. 5.13.   Two

capillary tubes a and b are selected, having internal diameters of about 0·3–0·4 mm and 1·5–2 mm respectively. They are cleaned with warm chromic acid, rinsed with clean water, and the capillary rise with water, h_w, is noted roughly for each. Marks are then scratched on the tubes at a distance say $(h_w+1$ cm$)$ above the end of each. This procedure ensures that, whatever the liquid to be tested, the tubes can always be lowered into the liquid until the meniscus stands opposite the mark. The tubes must next be calibrated with water or benzene—preferably the latter, unless aqueous solutions are to be studied.

The capillary tubes are mounted in a boiling tube c of good optical quality and supported in a cork as close together as possible so that they can be viewed simultaneously in the telescope of a vernier travelling microscope or cathetometer reading to 0·05 mm or better. The cork should provide a sliding fit so that the tubes can be raised or lowered.

Tubes a, b and c are thoroughly cleaned with chromic acid, washed well under a running tap, rinsed several times with rectified spirit and then twice with pure benzene. Parts of the glassware that will come into contact with the experimental liquid must not now be touched with fingers. The apparatus is assembled as shown, with a quantity of pure benzene in c, and the whole assembly is set up in a glass-sided thermostat or large beaker at $20·0\pm0·1°$ C. The capillaries are moved up or down until the meniscus in each is at the mark. The liquid is made to rise and fall in the capillaries by gently blowing or sucking through tube d so that the glass walls become wetted with benzene, thus ensuring a contact angle of zero. The liquid levels should return to an

Fig. 5.13. Determination of surface tension by the differential capillary rise method.

accurately reproducible position a minute or two after repetition of this treatment, otherwise a dirty tube is indicated. The final positions of the bottom surface of each meniscus is measured on a travelling microscope or cathetometer (set up precisely vertical). The liquid level in c is noted approximately on the same instrument. The two capillary rises, h_1 and h_2 need not be known to better than 0·1 mm but the difference (h_1-h_2) is measured as accurately as possible. These determinations complete the calibration of the tubes. The apparatus may now be cleaned and the measurements repeated in just the same way with the liquid of unknown surface tension.
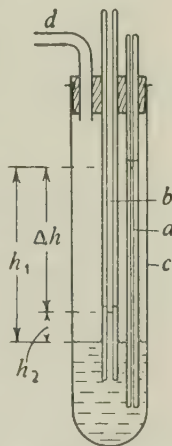
Calculation. The *elementary* theory of capillary rise equates the upward pull of surface tension, $2\pi r\gamma$ (r = internal radius, γ = surface tension) with the weight of the column of liquid (density ρ), $\pi r^2 h\rho g$, i.e. $\gamma = \frac{1}{2}rh\rho g$. Hence, for two tubes, $r_1 h_1 = r_2 h_2$, and the difference of level $\Delta h = (h_1 - h_2)$ $= \frac{\gamma}{\rho}\left[\frac{2}{g}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)\right]$. The term in square brackets is a constant for the apparatus, and is therefore obtained from the calibration. Hence, when measurements are made on another liquid of density ρ^1 and capillary difference $\Delta h'$, its surface tension follows at once as $\dfrac{\gamma'}{\gamma} = \dfrac{\Delta h'\rho'}{\Delta h\rho}$. When the differential method is used with this simple theory it gives results accurate to about 1%, which is rather better than would be obtained by the one-tube method. However, only a little further calculation is needed to obtain an accuracy of about 0·1% from the same data, as follows.

For greater accuracy the Poisson-Rayleigh formula can be used to allow for the weight of liquid contained in the meniscus. This correction is equivalent to addition of a small height to the capillary rise, h. The effective height, H, is given by

$$H = 2\gamma/r\rho g = h + r/3 - 0.1288 r^2/h + 0.1312 r^3/h^2$$

For tubes having $r < 0.2$ mm the last two terms are quite negligible, and even for tubes up to $r = 1$ mm the last term can be neglected if an accuracy of 0·1% is sufficient.

When these corrections are applied to the differential apparatus, the two capillary rises are given by $H_1 = 2\gamma/r_1\rho g = h_1 + r_1/3$ for tube a, and $H_2 = 2\gamma/r_2\rho g = h_2 + r_2/3 - 0.129 r_2^2/h_2$ for tube b. The differential height, Δh, is therefore given by

$$\Delta h = (h_1 - h_2) = \frac{2\gamma}{\rho g}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) + \frac{1}{3}(r_2 - r_1) - 0.129\frac{r_2^2}{h_2}$$

The approximate magnitudes of the 3 terms on the right-hand side with the present apparatus are 6·0, +0·03, and −0·0009 for water and 2·7, +0·03, and −0·002 for benzene. It is seen that the first correction term, $\frac{1}{3}(r_2 - r_1)(= B)$, is quite important, but r_1 and r_2 need not be known to better than 5% for an accuracy of 0·1% in Δh or γ. Consequently, r_1 and r_2 can be calculated sufficiently accurately from the uncorrected theory, i.e. $r_1 \approx 2\gamma/h_1\rho g$ and $r_2 \approx 2\gamma/h_2\rho g$, taking the known values of γ and ρ for the calibrating liquid. The procedure, therefore, is to calculate first r_1 and r_2 and then the two correction terms, and finally insert the accurate value of Δh in the working equation to obtain an *accurate* value for the constant term $(1/r_1 - 1/r_2)(= A)$. The apparatus is then fully calibrated and can be used in the same manner with a liquid of unknown surface tension (but known density ρ'). The capillary rises h_1' and h_2' are measured approximately but their difference, $\Delta h'$, accurately. The working formula is, as before,

$$\Delta h' = \frac{2\gamma'}{\rho'g}A + B - C \quad \text{(where } C = 0.129 r_2^2/h_2'\text{)}$$

Now A is known accurately from the calibration, while B and r_2 are known

sufficiently closely. Since the last term, C, is very small, h_2' need be noted only roughly.

It is possible, in fact, to dispense with measuring h_1' and h_2' separately and measure only $\Delta h'$. The calculation is then made by successive approximations as follows. First an approximate value of γ' (say γ'') is obtained by neglecting the C term and writing $\Delta h' \approx 2\gamma'' A/\rho' g + B$. Now since r_2 is known, the C term is given approximately by $-0\cdot129 r_2^2/h_2$ $= -0\cdot129 r_2^3 \rho' g/2\gamma''$. A corrected value of γ' (say γ''') is now calculated from the full equation, and if γ''' is significantly different from γ'' the C term can be recalculated and a new value, γ'''', obtained, the process being repeated until no further change in γ' is produced. Probably one recalculation will be enough to reach a constant value of γ' to within $0\cdot1\%$.

EXPERIMENT

Determine the surface tension of a pure organic liquid (e.g. ethyl acetate) by the differential capillary rise method at a series of temperatures from $20°$ to $50°$ C, and hence test the constancy of the parachor of the compound.

Procedure. Calibrate the apparatus with benzene at $20\cdot0°$ C as described above, taking its surface tension as $28\cdot88$ dynes/cm and density as $0\cdot8784$. Then carry out the measurements with the liquid, determining its density at the same temperatures with a pyknometer (or taking values from tables). Calculate the surface tension for each temperature and compare the values with published data. Hence calculate a series of values for the parachor of the substance and take a mean. Compare the result with the value calculated from Sugden's parachor constants given on p. 93.

B. Sugden's bubble-pressure method. When a bubble is formed slowly at a jet (radius r) which dips to a depth of h in a liquid (density ρ, surface tension γ), the pressure in the tube increases to a maximum which corresponds with a hemispherical bubble and then decreases as the bubbles break away. On simple theory, the maximum bubble pressure should be given by $(h\rho g + 2\gamma/r)$, and this may be measured on an external U-tube manometer. This is the basis of Jaeger's method. The theory, however, needs refinement to allow for the departure of bubble shape from hemispherical form,[2] and the method shares with capillary rise the difficulties associated with having a wide, plane, liquid surface (see above). These complications were overcome by Sugden [3] by using two jets at the same depth and calibrating the apparatus with a standard liquid. An empirical equation accurate to $0\cdot1\%$ was found, namely:

$$\gamma = A(P_1 - P_2)\left[1 + 0\cdot69 r_2 \frac{\rho g}{(P_1 - P_2)}\right]$$

where A is a constant of the apparatus, P_1 and P_2 are the pressures

(in dynes per sq. cm) required to form bubbles at the narrow and the wide jet respectively, and r_2 is the radius of the *wider* jet. The method is one of the most convenient for an accuracy of about 0·3%. The apparatus is shown in Fig. 5.14. The bubbler tube, A, contains the two jets at the same level, of radii $r_1 =$ about 0·1 mm and $r_2 = $ 1–2 mm. The jets are made by pulling down quill tubing, cutting off cleanly, and grinding on a glass plate with fine carborundum powder and water until the tips are smooth, sharp edged, and perpendicular to the sides. The bubbler is connected to the flask B and dropping funnel C containing mercury by means of which the pressure can be slowly increased. The pressure inside the tubes is measured on a U-tube manometer D containing a non-volatile liquid such as dibutyl phthalate (density 1·05 approx., but it should be
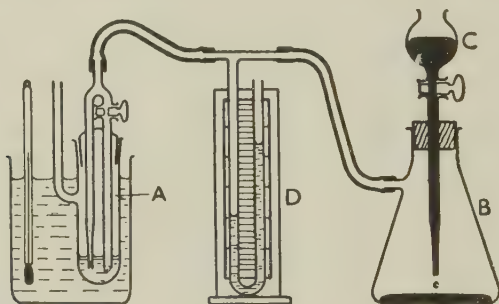
Fig. 5.14. Determination of surface tension by Sugden's maximum bubble-pressure method.

determined for the manometer temperature). The apparatus should, of course, be free from leaks.

To calibrate the apparatus, the bubbler and jets are first carefully cleaned and then rinsed with water, alcohol, and finally benzene. Enough pure benzene is poured into A to cover the jets to a depth of about 5 mm. Bubbles are formed *very slowly* at each jet in turn by increasing the pressure in the apparatus by running a slow stream of mercury from the dropping funnel C (the stem of which should be constricted and full of mercury). The rate of bubbling should not exceed about 1 bubble per second. The *maximum* bubble pressures are read on the manometer D by means of a cathetometer, lens and scale, or vernier calipers and corrected to dynes per sq. cm. The radius of the wider jet, r_2, must be measured with a travelling microscope, a mean of radii in several directions being taken. The constant of the apparatus, A in Sugden's equation above, can now be calculated. ($\gamma = 28·88$ and $\rho = 0·878$ for benzene at 20° C.)

Having determined the apparatus constant, A, the surface tension

of various liquids at any temperature may be determined readily as required, and their parachors calculated (p. 93).

C. The drop-size method. When a drop of liquid is formed *very slowly* at a jet (Fig. 5.15), the quantity of liquid which eventually falls off is a *definite* function of the radius of the jet, r, the density of the liquid, ρ, and its surface tension, γ, but it cannot be calculated from any *simple* theory. However, Harkins and Brown [4] (1919) made a very careful experimental study of drop sizes, and prepared tables which can be used to obtain surface tension with an accuracy of 0.1% from careful measurements of drop size. The surface tension is calculated from the formula $\gamma = F \times mg/r$ where m is the mass of a drop, and F is a factor depending on v/r^3, v being the volume of the drop. Some values of F are given in the following table.[10]
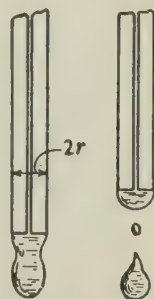
Fig. 5.15. Stages in the detachment of a drop from a jet.

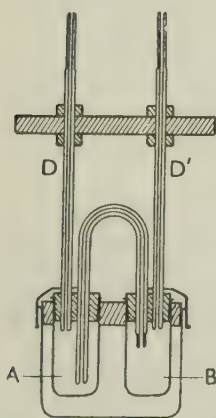| v/r^3	F	v/r^3	F	v/r^3	F
17·7	0·2305	3·433	0·25874	1·4235	0·26544
13·28	0·23522	2·995	0·26065	1·3096	0·26495
10·29	0·23976	2·637	0·26224	1·2109	0·26407
8·190	0·24398	2·3414	0·26350	1·124	0·2632
6·662	0·24786	2·0929	0·26452	1·048	0·2617
5·522	0·25135	1·8839	0·26522	0·980	0·2602
4·653	0·25419	1·7062	0·26562	0·912	0·2585
3·975	0·25661	1·5545	0·26566	0·865	0·2570

Fig. 5.16. Apparatus for determination of surface tension by the drop-weight method.

Apparatus similar to that of Morgan[5] (Fig. 5.16) is usually employed for measuring surface tensions by the drop-weight method. Liquid in bottle A is very slowly forced through the capillary tube to grow a drop on the special jet in bottle B. The drop must fall away by gravity only (not vibration or kinetic energy of flow). Some 30 drops are collected and weighed and the surface tension calculated by use of the above tables. (See references for other details.)

Interfacial tensions. The drop-size method is particularly suitable for measurement of *interfacial tensions* between two immiscible liquids. Further, since much larger drops are obtained than with drops in air, it is possible to measure their size volumetrically. A very convenient apparatus for measuring

small volumes accurately is the micrometer syringe* (Fig. 5.17 (a)), in which a graduated micrometer A propels the piston of a hypodermic syringe B of known cross section. This instrument reads down to 0·0001 ml and consequently the volume of one drop can be determined accurately. If a micrometer syringe is not available, a microburette readable to 0·001 ml can be constructed from a graduated 1 ml pipette (Fig. 5.17 (b)). In this microburette [6] the liquid is displaced by mercury, and the position of the mercury
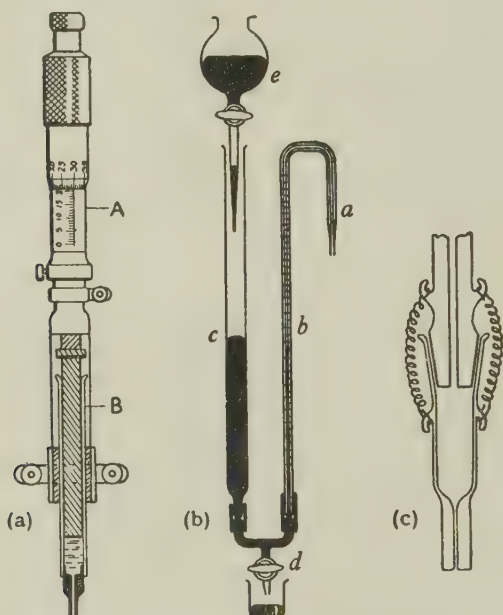
FIG. 5.17. Determination of drop-volume.
(a) Micrometer syringe (1 ml).
(b) Microburette (1 ml).
(c) Detachable jet for interfacial-tension measurements.

meniscus can be read very precisely. To charge the burette with the liquid, the jet a is dipped into a beaker of the liquid and *clean* mercury is run into the tube c from the dropping funnel e until it overflows through a. The tap d is then slowly opened, and as the mercury runs out it draws liquid behind it into the graduated limb b. The tap is closed when the liquid-mercury interface reaches the bottom of the scale. The liquid is delivered by running mercury

* The "Agla" micrometer syringe is obtainable from Messrs. Burroughs Wellcome and Co., Ltd., London.

into c from the tap funnel. As the bore of the tube c is much greater than that of b it is easy to control the movement of the mercury level, and a very slow rate of rise can readily be produced.

The jet used for interfacial tension determinations must be large if the v/r^3 value is to fall within the accurate range of the table of Harkins and Brown (namely, 10 to 0·8); for the water-benzene system an outside diameter of 7 to 10 mm and bore of about 0·4 mm are suitable. The jet should be ground truly cylindrical, and must certainly be ground accurately perpendicular at the end and the edges must be sharp. The diameter of the jet is measured by a travelling microscope. It is advisable to have the jet detachable from the burette, as shown in Fig. 5.17 (c).

To make a determination of interfacial tension, the jet is immersed in the less dense of the two liquids, and drops of the heavier liquid are slowly formed. The drop can be expanded fairly fast at first, but the delivery of the last 5% should take at least one minute. Clearly, the correct drop-volume (v) is not obtained unless the *previous* drop has also been correctly produced. The other quantity needed for the calculation is the effective density of the heavier liquid when suspended in the lighter, i.e. the difference between their densities $(\rho_1 - \rho_2)$. These should be determined very accurately by means of a pyknometer at the temperature used in the experiment. The interfacial tension, $_1\gamma_2$, can then be calculated from the expression $_1\gamma_2 = \dfrac{v(\rho_1 - \rho_2)g}{r}F$, the value of F being obtained from the v/r^3 function by interpolation of the tables.

EXPERIMENT

Determine the interfacial tensions of the benzene-water, chloroform-water, and medicinal paraffin-water interfaces. Discuss the results with reference to Antonoff's rule, namely,

$$_1\gamma_2 \approx {}_1\gamma_{\text{Air}} - {}_2\gamma_{\text{Air}}$$

D. The ring-detachment method (du Nouy[9]). For many purposes, e.g. study of biological fluids, colloidal solutions, etc., the surface tension can be determined quickly and with sufficient accuracy by measuring the force required to detach a horizontal ring of platinum wire (radius R) from the surface of the liquid. On the elementary theory, the force, P, should be given by twice the perimeter of the ring times the surface tension, i.e. $P = 4\pi R\gamma$ (see Fig. 5.18 (a)). More precisely, the pull must be multiplied by a correction factor, F, which has been determined experimentally by Harkins and Jordan[7] and theoretically by Freud and Freud.[8] F varies from 0·75 to 1·1, and depends on the dimensions of the ring (radius of ring R, radius

of wire, r) and the density and surface tension of the liquid.   The tables of Harkins and Jordan give values of F as a function of R/r and R^3/V, V being the volume of liquid raised ($=$ Force/$g \times \rho$). The following short table gives some values for the size of ring often used (du Nouy, 1926), having R/r about 42.

R^3/V	0·3	0·5	1·0	2·0	3·0
F	1·042	0·973	0·910	0·860	0·828

The apparatus employed is generally du Nouy's torsion balance (Fig. 5.18 (b)); a chainomatic balance is also suitable if means are provided for adjusting the level of the liquid.   Since it is not easy
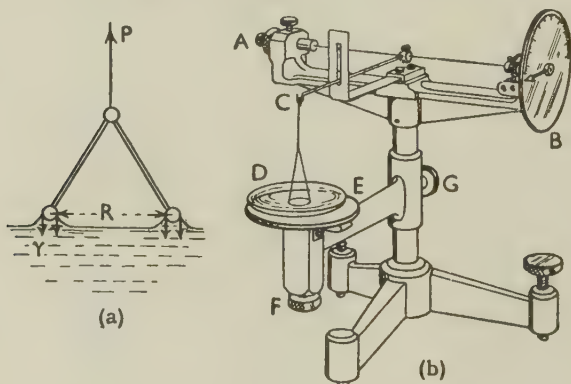
FIG. 5.18. Determination of surface tension by du Nouy's method.
(a) Principle of the method.   (b) Torsion balance.
(Courtesy Cambridge Instrument Co., Ltd., London.)

to adapt the apparatus for use at different temperatures, measurements should be made near room temperature, and the liquid should be brought to a definite temperature immediately before the measurement is made.   The method is appropriate when the surface tension of a large number of samples must be measured to the nearest 0·1 dyne, e.g. when studying the lowering of γ by surface-active solutes (Ch. 14).   The solutions can be made up in a series of flasks to be stood in a thermostat in readiness for the determinations.

Procedure.   The platinum ring is first thoroughly cleaned by means of a hot sulphuric acid and bichromate mixture, washed with distilled water and heated for a moment in an alcohol flame, or non-luminous Bunsen flame.   It is then suspended from the hook on

the beam C. The pointer B is set at zero and by means of the screw A, the torsion of the wire is adjusted so that the beam C lies in its normal, horizontal position just clear of the arm. The platform with dish containing the liquid under test is raised until the liquid just touches the ring. The knob which twists the wire is then turned slowly until the ring is suddenly torn from the surface of the liquid, and while this is being done the platform E must at the same time be lowered by means of the screw F so as to keep the beam C always in its normal horizontal position. The position of the pointer on the scale is read when the ring is torn from the surface of the liquid. Several determinations of this point should be made.

To obtain the value of the surface tension, the scale must be calibrated. This is done by determining the torsion of the wire with different known weights on the ring. A weighed piece of wire is placed on the ring and weights are added. For each load the wire must be twisted until the beam is in its normal position. The pointer reading on the scale is noted. If the torsion of the wire is proportional to the angle through which the pointer is turned, the weight divided by the scale reading will be the same in each case. If this is not so, the weights must be plotted against scale readings. If the weight in grams is multiplied by the force of gravity, the value in dynes corresponding to a given scale reading is obtained. The surface tension is calculated from the maximum pull by the equation $\gamma = PF/4\pi R$, the value of F being taken from the tables.

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[10] Reproduced by permission of the McGraw-Hill Book Co., Inc., from *International Critical Tables*, Vol. 4, Copyright 1928, McGraw-Hill Book Co., Inc.

CHAPTER 6

THERMODYNAMIC PROPERTIES OF DILUTE SOLUTIONS

DETERMINATION OF MOLECULAR WEIGHTS AND ACTIVITY COEFFICIENTS: CHEMICAL EQUILIBRIA IN SOLUTION

6A. INTRODUCTION: THE "COLLIGATIVE" PROPERTIES

Dilute solutions have played an important part in the history of physical chemistry because many of their properties are found to be closely related—at least as a first approximation—to the *molar* concentration of solute which they contain, and to depend relatively little on the nature of solute. Consequently, measurements of these properties have provided methods of determining *molecular weights* of substances in solution.

When a substance B is dissolved in a solvent A, the vapour pressure of A is reduced from its normal value, p_A°, to a lower value, p_A^s, which is given according to Raoult's Law by $p_A^s = p_A^\circ N_A$, where N_A is the *mole fraction* of A in the solution defined by

$$N_A = \frac{\text{no. of moles of } A}{\text{total no. of moles}}.$$

Solutions which obey this law at all concentrations are called *ideal*. In practice, Raoult's Law is found to hold approximately for solutions in which solute and solvent are of very similar chemical nature. More often, however, Raoult's Law holds only for the solvent, A, and then only for solutions that are very dilute in B (i.e. as $N_A \rightarrow 1$). In such solutions the solute, B, tends to follow Henry's Law, namely, $p_B = kN_B$, where k is a constant; or $p_B = p_B^\circ N_B f_B$, where f_B is the "activity coefficient" of B.

If w g of solute of (unknown) molecular weight m are dissolved in W g of solvent of (known) molecular weight M, the partial pressure of A over the solution is given by

$$p_A^s = p_A^\circ \frac{W/M}{(W/M + w/m)}$$

if the solution is ideal. Consequently, a study of the vapour pressure of the *solvent* can given information about the *molar* composition of the solution, and if the weight composition is known,

the molecular weight of the *solute* can be calculated. The lowering of the vapour pressure can be measured by the gas saturation method (Ch. 5), by a dew-point method (Ch. 7) or by the so-called "isopiestic" method in which the solution is brought to vapour equilibrium with solutions of a substance of known vapour pressure,[1] but although these methods are frequently used for studying the thermodynamic properties of solutions, they are rarely employed for molecular weight determinations. In place of the lowering of vapour pressure it is more convenient to measure the corresponding *elevation of the boiling point* (ΔT_b) or *depression of freezing point* (ΔT_f). The origin of these phenomena can be understood from the vapour pressure–temperature diagram (Fig. 6.1). The solution,

having a lower vapour pressure than the pure solvent (assuming solute *B* to be non-volatile), must be raised to a higher temperature to bring its pressure up to 1 atm, i.e. its b.p., and similarly the solution must be cooled to a *lower* temperature for its vapour pressure to coincide with that of the pure solid (i.e. its f.p.). It can be shown by thermodynamics that the elevation of the boiling point (the solute being non-volatile) or depression of the freezing point (assuming that pure solvent crystallizes out on cooling) for a

FIG. 6.1. Diagram showing the effect of a non-volatile solute in reducing the v.p., raising the b.p., and depressing the f.p. of a solution.

dilute solution in which the solvent obeys Raoult's Law are given by the same formula, namely:

$$\Delta T = \frac{RT^2}{L} \cdot N_B$$

where ΔT is the elevation (or depression), L is the molar latent heat of vaporization (or crystallization), and T is the boiling point (or freezing point) on the Kelvin scale. On rearrangement, the equation gives for the molecular weight of the solute $m = Kw/\Delta TW$, where $K(= RT^2M/L)$ is a constant for the solvent, known as the boiling point ("ebullioscopic") constant (K_b) or freezing point ("cryoscopic") constant (K_f) in the respective cases. The table overleaf gives the approximate values of these constants for some common solvents.

The f.p. depression is easier to measure accurately than is the b.p. elevation. It has therefore been used frequently for studying the
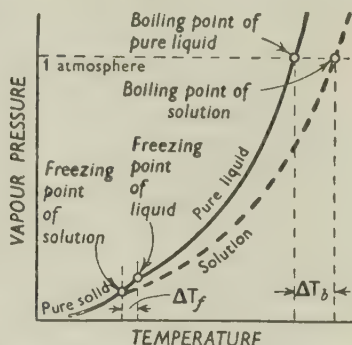
Solvent	f.p. (°C)	K_f	b.p. (°C)	K_b	Pressure* correction
Acetic acid	16·6	3,900	—	—	—
Acetone	—	—	56·2	1,710	4
Benzene	5·4	5,120	80·2	2,530	7
Chloroform	—	—	61·2	3,630	9
Ethyl alcohol	—	—	78·5	1,220	3
Nitrobenzene	5·3	7,200	—	—	—
Water	0·0	1,858	100·0	505	1

* The correction values in the last column are per 10 mm, and should be added to K_b when the barometric pressure is above 760 mm and subtracted when it is below 760 mm (see Hoy and Fink, *J. Phys. Chem.*, 1937, **41**, 453).

behaviour of solutes which give abnormal results for "molecular weights" on account of *association* (e.g. carboxyllic or hydroxy-compounds in benzene), *dissociation* (e.g. salts in water), hydration, or complex formation (e.g. $AgNO_3 + NH_3$, $KBr + HgBr_2$). Ideally, the method provides means of counting the total number of molecules or ions in the solution, since ΔT gives N_B, the mol. fraction, but the theory is limited to solutions which are more or less ideal. Electrolytes, in particular, are grossly non-ideal because the coulombic interaction between the ions has an important influence even in dilute solutions, and consequently the above theory does not hold. Instead, measurements of freezing point depression are used to study empirically the activity coefficients of electrolyte solutions.[2]

Osmotic pressure. Another property which is closely related to those discussed above is the *osmotic pressure*.[3] This is the hydrostatic pressure which must be applied to the solution to bring its vapour pressure up to that of the normal pure solvent. The osmotic pressure of very dilute, ideal solutions is given by $\pi = nRT/V$, where n is the number of moles of solute dissolved in a solution of volume V. Osmotic pressure therefore provides another means of determining molecular weights. However, the technique—especially the preparation of semi-permeable membranes—is difficult and outside the scope of this book. The method is used for high polymers and proteins; measurements are made at a series of concentrations and extrapolated to infinite dilution to eliminate the effect of non-ideality of the solutions.[3]

In recent years the *scattering of light* by solutions has been shown to be related to their osmotic pressure, and an important new method of determining molecular weights has been developed.[4]

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[3] For technique of osmometry see Weissberger, Vol. 1, Pt. 1, Ch. 11.

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6B. DEPRESSION OF THE FREEZING POINT

1. Beckmann's (supercooling) method. The principle of the classical method developed by Beckmann is to find the arrest that occurs in the cooling curve of the solution, corresponding to the onset of crystallization of solid.   The solution is cooled very slowly by a freezing mixture.   Crystallization usually does not begin until the temperature has fallen a little below the true freezing point, i.e. the solution supercools, but as soon as nuclea-

tion has taken place the latent heat of crystal-
lization tends to raise the temperature.   The
temperature cannot rise above the freezing
point, but if the cooling is too rapid it may
well never reach the true melting point.   The
proper experimental technique must therefore
be adhered to closely to obtain reliable results.

Apparatus (Fig. 6.2).   The solution is con-
tained in the freezing-point tube *C* which has a
side tube *D* for insertion of the solute, and is
fitted with a sensitive thermometer *T* (see below)
and a stirrer *S*, to the upper end of which a non-
conducting handle of cork or wood is attached.
The stirrer passes through a short piece of
glass tubing inserted in the cork of the freezing-

FIG. 6.2. Beckmann's
f. p.   depression
apparatus.

point tube so that it moves freely.   The tube *C* is supported by a ring of asbestos inside a wide boiling tube *B* which serves as an air-mantle separating *C* from the freezing bath.   This ensures a slower and more uniform rate of cooling of the liquid.   The freezing bath is contained in a glass jar *A*, on top of which rests a lid of brass or, better, plastic.   The lid has a central hole to take the tube *B* and also holes for a stirrer *E* and thermometer.
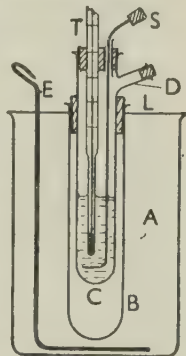
The Beckmann thermometer.   In order that the determination of the depression of the freezing point can be made with sufficient accuracy, it is necessary to be able to read the temperatures with an error not exceeding $0.001-0.002°$.   A Beckmann thermometer is therefore used.   This instrument has a large bulb and a range of only five or six degrees.   It is graduated in $0.01°$ and can be read to the nearest $0.001°$ with the aid of a special lens.   It does not

indicate absolute temperatures, but merely differences of tempera-
ture. The special feature of the Beckmann thermometer is that the
amount of mercury in the bulb can be adjusted to make the thermo-
meter read at any desired region of temperature. The regulation is
effected by transferring some mercury into a small reservoir at the
upper end of the capillary, or vice versa. Clearly, the lower the
temperature for which the thermometer is required to read, the
greater must be the quantity of mercury in the bulb.

WARNING. *Beckmann thermometers are very fragile and expensive
and must therefore be handled with special caution. They should
always be returned to their case when out of use, and particular care
is needed when mounting the thin outer sheath in a clamp or other
support.*

Setting the Beckmann thermometer. Before using the Beckmann
thermometer, it must be "set", i.e. the amount of mercury in the
bulb must be adjusted so that at the particular temperature of the
experiment the end of the mercury thread is on the scale. This is
done as follows.

First hang the thermometer in a beaker of water which has been
adjusted, with the aid of an ordinary thermometer, to the temperature
at which the experiment is to be conducted, and see whether or not
the top of the mercury of the Beckmann thermometer stands on the
scale. If it does not, then suppose in the first place that it does not
rise as far as the scale; that is, suppose there is too little mercury in
the bulb. In this case, place the thermometer in a bath the tempera-
ture of which is sufficiently high to cause the mercury to pass up to
the top and to form a small drop at the end of the capillary. Now
invert the thermometer, and tap it gently so as to collect the mercury
in the reservoir at the end of the capillary and to join with the mer-
cury there. Return the thermometer carefully, without shaking,
to the upright position, and place the bulb again in a bath, regulated
for the required temperature. Since the scale of the Beckmann
thermometer does not extend upwards to the end of the capillary,
the temperature of this bath must be at least 2–3° *higher* than the
highest temperature to be met with in the experiment. The mercury
in the bulb will contract and draw in more mercury from the
reservoir. After several minutes, when the thermometer will have
taken the temperature of the bath, strike the upper end of the
thermometer gently against the palm of the hand so as to cause the
excess of mercury to break off from the end of the capillary. Make
sure, now, that the amount of mercury has been properly regulated,
by placing the thermometer in a bath at a temperature which is equal
to the highest that will occur in the experiment, and see that the
mercury stands on the scale. If it stands above the scale, too much

mercury has been introduced, and some of it must be got rid of by driving the mercury once more up into the reservoir and shaking off a little of it from the end of the capillary. Of course, if the mercury is found to stand too low on the scale, then more mercury must be introduced into the bulb in the manner described above, these operations being repeated until the proper amount of mercury has been introduced. *This must always be tested by placing the thermometer in a bath at the temperature of the experiment and making sure that the mercury remains on the scale.*

On account of the so-called "thermal after-effects" met with in the case of glass, owing to which glass, after being heated, does not immediately acquire its original volume, it is advisable to have at least two Beckmann thermometers, one for use at lower, the other for higher temperatures. Also, it is worth mentioning that it is often possible to get the mercury to pass from the bulb to the reservoir or vice versa simply by inverting the thermometer and tapping it gently. This avoids heating the thermometer.

Precautions which should be observed in carrying out determinations by the supercooling method:

(i) *The temperature of the cooling bath must not be too low*, otherwise the supply of heat by crystallization of the solvent may not be great enough to counteract the abstraction of heat by the cooling bath. In practice, the temperature of the cooling bath should not be more than $3°$ or $4°$ below the freezing point of the liquid.

(ii) *The amount of supercooling should not exceed 0.3–$0.5°$*. If a larger amount of supercooling occurs, so large is the quantity of solid which eventually separates that the concentration of the solution is thereby appreciably increased, with consequent spurious further depression of the freezing point. When the solution has supercooled by about $0.1°$ it is stirred vigorously to encourage crystallization to begin. If this does not succeed, the solution must be "seeded" by adding a small crystal of frozen solvent. Another method is to insert into the solution a wire which has been cooled to a low temperature (e.g. with solid CO_2).

(iii) *The stirring should not be too rapid and should be as uniform as possible* otherwise too much heat is generated. An up-and-down movement of the stirrer at the rate of about once per second is sufficient.

(iv) *The thermometer should always be tapped before a reading is taken.* As the bore of the thermometer is very narrow, the mercury is apt to "stick", and the object of tapping the thermometer gently with the finger or a small padded "hammer" is to overcome this hysteresis of the meniscus.

EXPERIMENT

Determine the molecular weight of a substance from its depression of the f.p. of benzene.

Procedure. First set up the apparatus (p. 107) completely, and see that the stirrer in the f.p. tube works smoothly without striking against the bulb of the thermometer. Remove the thermometer and stirrer from the f.p. tube, and fit the latter, which must be clean and dry, with an unbored cork. Weigh this tube, and then pour in 15–20 g of *pure* benzene, and weigh again. For this purpose a balance weighing to a centigram should be used. Now set the Beckmann thermometer so that at the temperature of 5·4° (m.p. of benzene) the mercury stands not lower than the middle of the scale. Dry the thermometer thoroughly and insert it, along with the stirrer, in the f.p. tube, so that the bulb of the thermometer is completely immersed in the benzene. Fill the vessel *A* with water and ice, so that a temperature of about 2–3° is obtained. This can be regulated by varying the amount of water and ice. The f.p. of the benzene is then determined.

In doing this, make a first approximate determination by placing the f.p. tube directly in the cooling bath, so that the temperature falls comparatively rapidly. When solid begins to separate, quickly dry the tube and place it in the air-mantle in the cooling bath; stir slowly and read the temperature when it becomes constant. Now withdraw the tube from the mantle and melt the solid benzene by means of the hand. If in this operation the temperature of the liquid is raised more than about 1° above the f.p., place the tube again directly in the cooling bath and allow the temperature to fall to within about half a degree of the f.p. as determined above; quickly dry the tube and place it in the air-mantle and allow the temperature to fall, stirring slowly all the while. When the temperature has fallen to about 0·2°–0·5° below the approximate f.p. found above, stir more vigorously. This will generally cause the crystallization of the benzene to commence, and the temperature will begin to rise. (If not, "seed" with a crystal of frozen solvent.) Stir slowly again, and with the help of a lens, read the temperature every few seconds, tapping the thermometer firmly with the finger each time before doing so. Note the highest temperature reached. Again melt the solid benzene which has separated out, and re-determine the f.p. in the manner just described. Not fewer than three concordant readings of the f.p. should be made, the mean of these being then taken as the f.p. of the benzene. The deviations of the separate readings from the mean value should not exceed 0·002°.

The f.p. of the solvent having been determined, a weighed amount

of the substance (e.g. camphor, naphthalene), compressed into tablet form, is now introduced into the benzene through the side tube D of the apparatus. The amount taken should be sufficient to give a depression of the f.p. of not less than $0.2°$. After the substance has dissolved, the f.p. of the solution is determined in exactly the same manner as described for the pure solvent, first an approximate and then not fewer than five accurate determinations being made. In each case note the degree of supercooling.

Two further additions of the substance should be made, and the f.p. of the solution determined after each addition. The total depression of the f.p. should not exceed about $0.5°$. From each set of determinations, calculate the molecular weight of the solute. The error should not exceed 3–5%.

Abnormal molecular weights

EXPERIMENT

In the manner previously described, determine the apparent molecular weight of benzoic acid in benzene, and from the numbers obtained calculate the degree of association, assuming that two single molecules combine to form one compound molecule.

Calculation. The degree of association can be calculated in the following manner: If x represents the degree of association, or the fraction of the total number of molecules which combine to form larger molecules, and if n represents the complexity of the new molecules, then of each mole of substance taken there will be $1-x$ mole unassociated, and x/n mole associated. Consequently, instead of there being 1 gram-molecule there will be only $(1-x+x/n)$ or $[1-x(1-1/n)]$. In other words, the number of dissolved molecules has decreased in the ratio of $1 : 1-x(1-1/n)$. The depression of the f.p. is proportional to the number of moles (in a given weight of solvent); hence, if d_t represents the depression calculated on the assumption of no association, and d_0 the depression actually obtained—

$$\frac{d_0}{d_t} = \frac{1-x(1-1/n)}{1}, \text{ or } x = \frac{d_t-d_0}{d_t(1-1/n)}$$

2. The equilibrium method. Instead of slowly freezing a solution of known concentration one can bring a solution to equilibrium with excess of pure frozen solvent and determine the temperature and concentration of the equilibrium mixture. This method is particularly suitable for aqueous solutions, and is capable of giving very high accuracy.[1] The determinations are best carried out in a Dewar vacuum vessel of 200–250 ml capacity, closed by a rubber stopper through which pass a Beckmann thermometer and a stirrer. A glass tube, wide enough to allow the passage of a pipette, also passes through the rubber stopper. While the experiment is in

progress, this tube is plugged with cotton-wool. The Dewar vessel is packed in a wooden box with cotton-wool. The box should also be closed by a lid pierced with holes for the thermometer and stirrer, and for the passage of a pipette. Distilled water, sufficient in amount to cover the bulb of the thermometer, is placed in the Dewar vessel which is then practically filled with broken ice prepared from distilled water. The contents of the vessel are stirred and the equilibrium temperature read as carefully as possible on the Beckmann thermometer. The water is then poured away and about 100 ml of 0·2–0·3 molal solution, previously cooled to 0° by standing in a jar of ice, are poured into the Dewar vessel. More pure crushed ice is added if necessary. When the temperature has become constant, 20–25 ml of the solution are withdrawn by means of a fine-pointed pipette, and run into a small weighed flask. The weight of the solution is determined and its concentration then ascertained by titration or by gravimetric analysis or by a physical method of analysis such as determination of the refractive index, conductivity, or absorption of light.

Calculation of osmotic coefficients and activity coefficients from freezing point data for dilute solutions

Solvent activity. In the first instance, a freezing point depression gives a measure of the *activity* of the solvent in the given solution at its freezing point (T)

Provided the solution is so dilute that the heat of dilution is negligible, it can be shown that the activity of the solvent in the solution $(a_1)_T$ relative to that of the pure solvent, is given by

$$\log_e (a_1)_T = - \int_T^{T^\circ} \frac{L_f}{RT^2} \mathrm{d}T$$

where L_f is the molar heat of fusion of the pure solid solvent, T° is the f.p. of the pure solvent, and T is that of the solution. L_f is itself dependent on temperature, and can be expressed in terms of T by means of the Kirchhoff equation, thus,

$$(L_f)_T = (L_f)_{T^\circ} + (C_p^S - C_p^L)(T^\circ - T)$$

where C_p^S and C_p^L are the molar heat capacities of the pure solid and liquid respectively.

In the case of water, $(L_f)_{T^\circ}$, the heat of fusion at $0°$ C, is 1,438 cal, and $(C_p^S - C_p^L)$ is -9 cal per degree. Hence, putting the change of f.p. as $\Delta T = T^\circ - T$, it follows as a first approximation

$$\log_e (a_w)_T = -0.009696\ \Delta T - 0.0000051\ (\Delta T)^2$$

Measurements of the f.p. depression, ΔT, therefore give at once the activity of the solvent, $(a_1)_T$.

If the solution were ideal, according to Raoult's Law a_1 would be equal to the mol fraction of solvent in the solution, N_1.

Osmotic coefficients. For *non-ideal* solutions it is often convenient to discuss the thermodynamic behaviour of the solvent in terms of its *osmotic coefficient, g_1* (introduced by Bjerrum*), which is defined by $a_1 = (N_1)^{g_1}$. If the molecular weight of the solvent is M, and the total *molality* (moles per 1,000 g of solvent) of solutes in the solution is m, then, for a dilute solution, it follows to a good approximation

$$\log_e a_1 = g_1 \log_e (N_i) = -g_1 M_1 m/1{,}000$$

Clearly, an ideal solution corresponds to $g = 1$. For non-ideal solutions $(1-g_1)$ is a convenient measure of the deviation from ideality.

For the important case of an aqueous solution of an electrolyte of molality m which dissociates into ν ions per molecule, it follows that the osmotic coefficient of the water g_w is given by

$$g_w = -55{\cdot}51 \log_e a_w/\nu m$$

Substituting for $\log_e a_w$ in terms of the f.p. depression,

$$g_w = [0{\cdot}5382\Delta T - 0{\cdot}00028(\Delta T)^2]/\nu m \quad \ldots \ldots \ldots \text{(1)}$$

Activity coefficients. The osmotic coefficient of the solvent, g_1, is related to the "practical" activity coefficient of the solute, γ_2, through the Gibbs-Duhem relation. For a binary solution containing n_1 moles of solvent species (1) and n_2 moles of solute (2)

$$n_1 d(\log a_1) + n_2 d(\log a_2) = 0$$

Putting $\log a_1 = -g_1 m_2 M_1/1{,}000$ and $a_2 = \gamma_2 m_2$ leads to the equivalent form

$$-d \log \gamma_2 = -dg_1 + (1-g_1)d(\log m_2)$$

On integration from infinite dilution (where $\gamma = g = i$) to molality m, this gives

$$-\log \gamma_2 = (1-g_1) + \int_0^m (1-g_1)d(\log m)$$

In principle, therefore, γ for the solute at molality m can be obtained from f.p. depression determinations made on a series of solutions from infinite dilution up to m, the integral being obtained graphically. In practice, the relative error incurred in f.p. measurements on extremely dilute solutions excludes the possibility of obtaining accurate results by this procedure. Consequently, it is usual to assume some suitable form of law to govern g in extremely dilute solutions, and to perform the above integration only over the range of solutions which can be studied experimentally with accuracy. Thus, if the activity coefficient at molality m' is γ' (supposed known) then its value, γ'', at another molality m'' is obtained from

$$\log_{10} \frac{\gamma'}{\gamma''} = (g'-g'')/2{\cdot}303 + \int_{m'}^{m''} (1-g)d(\log_{10} m) \quad \ldots \ldots \text{(2)}$$

* Bjerrum's g = van't Hoff's i/ν = Lewis and Randall's $(1-j)$.

Electrolytes. The above equations apply equally to a solute which is an electrolyte as to one which is a non-electrolyte; in the former case, γ is the mean ion activity coefficient (cf. p. 242). However, the osmotic behaviour of salts in extremely dilute solutions is entirely different from that of non-electrolytes. Henry's Law is the limiting law for non-electrolytes—i.e. $a_2 \propto m_2$, which corresponds to $\gamma_2 = $ const. or $(1-g_1) \propto m_2$. For electrolytes, the limiting law is that of Debye and Hückel (cf. p. 242), according to which $-\log \gamma_{\pm}$ (or $1-g$) is proportional to $\sqrt{m}$. By assuming appropriate interpolation formulae, the range between infinite dilution and the lowest experimentally accessible concentration can be included in the above integration.[2]

EXPERIMENT

Determine the osmotic coefficients (and activity coefficients) of solutions of an electrolyte (e.g. hydrochloric acid) from about 0·01 N to about 1 N by the equilibrium f.p. method.

Procedure. Prepare some pure ice, break it into small pieces, and half-fill a Dewar vessel with it. Add enough distilled water, previously cooled to 0° C, to just fill the interstices of the cracked ice. Insert a Beckmann thermometer set so that the ice-point reads near the top of the scale, and stir up the ice and water until a steady reading is recorded.

Now add some pure hydrochloric acid (also previously cooled to 0°) and obtain a new equilibrium f.p. Note the steady temperature which is reached, and then take a sample of the equilibrium solution by means of a pipette with a fine point. If the solution is very dilute, at least 100 ml should be taken for analysis. Determine the concentration of the solution by titration as accurately as possible. (As the end-point of iodine titrations is sharper than that of acid-alkali titrations in the case of dilute solutions, it is advantageous to determine the acid by running it into an excess of a $KI–KIO_3$ mixture and titrating the iodine liberated with $Na_2S_2O_3$, using starch at the end-point. If desired, the chloride present could be determined instead by a potentiometric titration (p. 289).)

Now make a second addition of HCl. Obtain a new equilibrium temperature and take a sample of the liquid for analysis. Continue making additions of HCl to obtain further values of the f.p. at increasing concentrations until a depression of 2–3 degrees is reached.

Treatment of results. Calculate the osmotic coefficients of the solutions by use of equation (1) given above, taking $\nu = 2$ for HCl. Plot a graph of g against $\sqrt{m}$. Note that the experimental error on g becomes excessive for very dilute solutions. However, it is known that $g \rightarrow 1$ as $\sqrt{m} \rightarrow 0$, and, further, the line for g on the graph becomes asymptotic to the limiting law of Debye and Hückel in extremely dilute solutions, namely, for a 1 : 1 electrolyte in water at 0° C,

$$1-g = 0\cdot 374\sqrt{m}$$

Plot this line on the graph, and interpolate the line for g. Use the smoothed curve for the following exercise in the calculation of activity coefficients. (It will be appreciated that f.p. data of extremely high accuracy are called for in this field.[1])

It may safely be assumed that solutions of HCl conform fairly closely to the Debye-Hückel equation up to concentrations of 0·001 molal. At this concentration the activity coefficient (for 0° C) is given (p. 242) by

$$-\log_{10}\gamma_{\pm} = 0 \cdot 488\sqrt{m}$$

Compute values of $\gamma_{\pm}$ for 0·01, 0·05, 0·1, 0·5, and 1 molal by graphical integration of equation (2) above, plotting $(1-g)$ against $\log_{10} m$ from $m = 0 \cdot 001$ upwards.[3]

Other applications. Solutions of H_2SO_4 give much lower values of g than those for HCl. This is partly because of the effect of the divalent SO_4^{--} ions, and partly because the second stage of dissociation, $HSO_4^- \rightarrow H^+ + SO_4^{--}$, is weak.

Colloidal electrolytes, such as dodecyl sulphonic acid,[4] behave as normal electrolytes in extremely dilute solutions, but above a certain concentration (the critical micelle concentration) further increase of concentration lowers the f.p. very little, and g falls to abnormally low values. This is due to aggregation of the molecules into colloidal micelles, with the result that the number of osmotically active particles is much less than that calculated on the assumption of complete dissociation.

F.p. determinations on weak acids such as acetic can be used to deduce dissociation constants provided allowance is made for the activity coefficients of the ionic species (cf. p. 288).

3. Rast's micro-method of determining molecular weights. The basis of Rast's method of determining molecular weights is the use of *camphor* as a solvent.[5] The f.p. depression constant, K_f, of camphor is exceptionally large, namely, about 40° C for 1 mole of solute in 1,000 g of solvent, as compared with 5° for benzene and 1·86° for water. Consequently, a 10% solution in camphor may have a m.p. many degrees lower than that of pure camphor, and the depression can be measured sufficiently accurately with an ordinary thermometer instead of a Beckmann thermometer. By using a micro m.p. method, the determination of molecular weight can be carried out with as little as 0·2 mg of solute. Such small quantities have, of course, to be weighed on a micro-balance; if an ordinary analytical balance, weighing to $\pm 0 \cdot 1$ mg is used, the minimum quantity of substance required will be 10 mg since this can be weighed to the nearest 1%, which is the limit of accuracy expected of the method.

"Camphor" is not a unique substance. The common variety is either Japan camphor, which is *d*-2-camphanone ($C_{10}H_{16}O$, m.p. 178–179°, $[\alpha] = +44 \cdot 26°$), or artificial camphor (*dl*-). "Camphor" from Borneo, Malaya or Sumatra is *d*-borneol ($C_{10}H_{17}OH$, m.p. 208°, $[\alpha] = +37 \cdot 4°$). Commercial samples vary slightly in m.p. and optical rotation. Camphor is too waxy to be ground to a powder *dry*, but is easily ground when moistened with ether. Owing to the variable character of samples of camphor it is necessary to determine the m.p. and the f.p. depression constant of the camphor used in every experiment. Acetanilide (mol. wt. 135·1) or

naphthalene (mol. wt. 128·1) are suitable substances for calibration. In view of the necessity of making this standardizing measurement as well as the determination of m.p. of the pure camphor, there is no need to apply emergent stem corrections if all the temperatures are taken on the same thermometer.

Camphor is a good solvent for many substances. In using it to find molecular weights the implicit assumption is made that dilute solutions in camphor are "ideal", and, further, that the camphor crystallizes out first on cooling, since the simple f.p. depression theory does not apply when solid solutions or eutectics, or compounds separate. The validity of these assumptions has apparently never been proved. In practice, results within 5% are generally obtained. The method cannot be used for substances which are insoluble in camphor, react with it chemically, or decompose when heated to the m.p. of camphor. It has been applied successfully to liquid solutes.

EXPERIMENT

Determine the f.p. depression constant of camphor using acetanilide as solute at three concentrations, about 5, 10, and 20% by weight. Hence calculate the latent heat of fusion of camphor in calories per gram.

Preparation of the solution. Prepare a thin-walled glass tube about the size of an ignition tube (say about 1×5–10 cm), one end being pulled off and rounded by blowing into a slight bulb. Dry the tube in the oven, cool it, and weigh it as accurately as possible (± 0.1 mg). By means of a "micro-spatula" (i.e. a wire or thin glass rod flattened at one end) introduce about 10 mg of the substance to be used as solute into the bottom of the tube and weigh again. Now add about 100 mg of camphor and weigh a third time.

Before the contents of the tube are melted to form a uniform mixture, the open end of the tube must be sealed off and pulled out to a long, stout fibre to prevent volatilization of camphor. The tube is now placed in a small bath of high-boiling paraffin oil heated to the melting point of camphor, and when melted the contents are thoroughly mixed by rotating the tube, which is then left to cool in the bath. This precaution is to prevent condensation of camphor on the upper part of the tube, which might otherwise occur.

Determination of a melting point. When a homogeneous solution has been made and cooled, open the tube and introduce some of the contents into a thin-walled m.p. capillary ready for the determination of its m.p. The capillary is made by drawing down a thin glass tube such as an ignition tube, which should be absolutely clean. The final capillary should be about 2 mm wide at the bottom, 4–5 cm long, and sealed neatly at the bottom without a large bead of glass. Particles of solid are introduced by means of a fine glass ramrod. Prepare a similar capillary with pure camphor. Attach the capillary

tubes to the sides of a suitable thermometer by means of a thin rubber band (cut from the end of a piece of rubber tubing). The particles of solid should lie alongside the thermometer bulb. Several m.p. tubes may be run at the same time. The procedure is now the usual one commonly employed for finding the m.p. of organic solids. High-boiling paraffin or glycerol may be used as heating bath, and a small beaker or a "Cavalier flask" is a convenient container.

Clamp the thermometer with its attached capillary tubes so that the bulb and samples are just immersed in the heating bath. Raise the temperature rapidly to the neighbourhood of the m.p., and then warm *very slowly* with thorough stirring. A light glass-rod stirrer and a micro-burner may be used. Watch the samples closely. Near the m.p. the particles take on the appearance of melting ice, but still contain skeleton crystals. The point to be noted is the temperature at which the last crystals just disappear. Record this temperature as accurately as possible. The point when crystals first appear on *slow* cooling may also be determined. The measurements of m.p. and f.p. should be repeated several times until concordant results are obtained before dismantling the apparatus.

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6C. ELEVATION OF THE BOILING POINT

The true b.p. of a liquid is the temperature at which its vapour and liquid are in equilibrium under a pressure of 1 atm. This temperature cannot be determined accurately by simply inserting a thermometer into the boiling liquid, as the temperature in the liquid is variable and too high on account of local superheating and the effect of hydrostatic pressure. In the case of a *pure* liquid the *condensation* temperature can be determined instead by placing a thermometer in the condensing vapour, but in the case of solutions this method is not applicable since the condensation temperature then differs from the b.p. owing to fractionation.

One solution to the problem is to heat the liquid to its b.p. by means of a current of vapour (Landsberger's method). This method

eliminates superheating, but the concentration of the solution is thereby altered and must be determined subsequently.

All modern forms of apparatus make use of a principle introduced by Cottrell (1919); the thermometer is hung *in the vapour* above the boiling solution and a stream of boiling liquid is sprayed by a simple "pump" on to the thermometer *above the bulb*. The liquid is slightly superheated (e.g. by about 0·05°) when it emerges from the pump, but in flowing down the thermometer it very quickly comes to equilibrium with the surrounding vapour, cooling slightly by
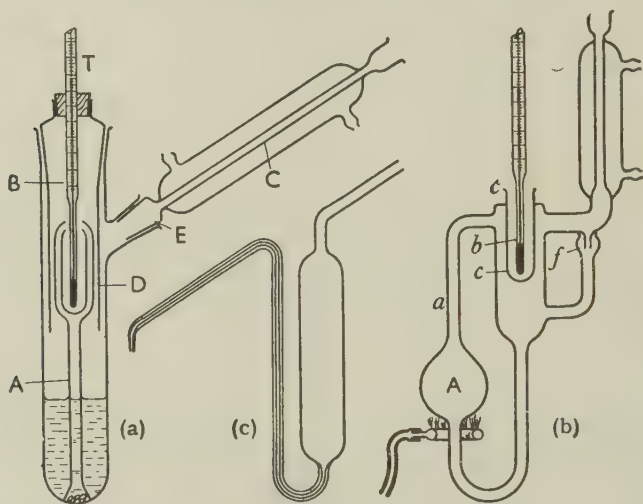
FIG. 6.3. Determination of elevation of the b.p.
(a) Apparatus of Washburn and Read.
(b) Apparatus of Swietoslawski.
(c) Weight delivery pipette.

evaporation.   The liquid dripping from the bulb is therefore at its true b.p.

Two forms of b.p. apparatus ("ebulliometers") are shown in Fig. 6.3: (a) is the apparatus of Washburn and Read,[1] and (b) is the basic form of ebulliometer favoured by Swietoslawski.[2]   In both types of apparatus the boiling liquid is carried upwards by the stream of vapour bubbles through a narrow tube A, a (the "pump" or "lift") so that liquid squirts continually on to the thermometer stem B or inserted well c into which the thermometer is dipped.   In the former apparatus the lift divides into two or three branches symmetrically arranged round the thermometer.   The tube D is to act as a radiation screen round the thermometer and to keep off cold liquid which may run down the condenser C.   Swietoslawski's

ebulliometer incorporates a drop-counter f which indicates the rate at which the liquid is distilling. Although originally heated by gas, either ebulliometer can be adapted for electric heating, and this has the advantage of being less disturbed by draughts, and gives closer regulation and reproducibility.

EXPERIMENT

Determine the molecular weight of a substance of low volatility by the ebullioscopic method, e.g. camphor, anthracene, or ethyl benzoate in benzene, or azobenzene in chloroform.

Procedure. A suitable amount of pure solvent is placed in the clean, dry boiling vessel, the quantity being determined by weighing. A weighed delivery pipette similar to that shown in Fig. 6.3 (c) may conveniently be used. The apparatus is assembled and wrapped with asbestos paper. If gas heating is used, a small burner capable of good regulation should be employed and protected from draughts by asbestos boards. The Beckmann thermometer is set to the tempera-ture at which the solvent boils and the apparatus is then assembled, and the solvent is brought to the boil.

It is essential to adjust the rate of boiling to the optimum. If the ebulliometer is functioning correctly there ought to be an appreciable range over which the heating can be altered without any change in thermometer reading, and the middle of this range should be used. It is therefore necessary to make some preliminary readings of temperature at different heating rates, the latter being noted, for example, by the setting of the gas-heating control or by the current passing (if electric heating is used) or by the rate of fall of drops from the condenser. For example, it may be found that the thermometer reading remains unchanged over the range 10 to 20 drops per minute; 15 drops per minute would therefore be chosen. Once the optimum rate of heating has been found, it should be closely adhered to throughout the subsequent work.

After the b.p. of the pure solvent has been found, a weighed pellet of solute (prepared in a tablet press) is introduced by way of the condenser, and the new b.p. is determined exactly as before. Further pellets may be added subsequently if several concentra-tions are to be studied.

The above readings can be used to calculate the molecular weight of the solute, assuming the theoretical value of the b.p. elevation constant. The result, however, is subject to two experimental errors; firstly, the solution is slightly more concentrated than when it was made up because a small, unknown amount of solvent is present in the condenser, and secondly, the graduations on the Beck-mann thermometer may not be precisely equal to centigrade degrees.

A rough correction for the first error is to subtract 0·2 g from the weight of solvent in making the calculations. A better method is to calibrate the ebulliometer with a solute of known molecular weight and use the empirical elevation constant so obtained in subsequently studying the elevation produced by the solute of unknown molecular weight. If the solutes are of similar chemical type, this comparative procedure will also tend to eliminate errors due to deviations from Raoult's Law. The same rate of boiling must obviously be used throughout.

Pressure correction. One difficulty that militates against more widespread application of ebulliometry is the sensitivity of the b.p. to changes of barometric pressure; changes are liable to occur while a series of measurements is in progress. The pressure-dependence of the b.p. can be calculated from the Clapeyron-Clausius equation in the form $\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{PL}{RT^2}$. P now becomes the barometric pressure, B, and T is the b.p. Hence, $\frac{\mathrm{d}T}{\mathrm{d}B} = \frac{RT^2}{LB} = \frac{K_b}{MB}$, where K_b is the b.p. elevation constant (p. 106) and M the molecular weight of the solvent. Hence, a change of barometric pressure equal to dB produces a change of b.p., $\mathrm{d}T = \frac{K_b\mathrm{d}B}{MB}$. The following list gives the increase of the normal b.p. ($B = 760$ mm) of some common solvents produced by an increase of barometric pressure of 1 mm: acetone 0·039°, benzene 0·043°, carbon tetrachloride 0·044°, chloroform 0·042°, ethyl alcohol 0·033°, methyl alcohol 0·033°, water 0·037°. It is seen therefore that if the thermometer reads to 0·001°, a significant change will be noticed if the barometric height varies by as little as 0·025 mm.

For ebullioscopic measurements of high accuracy it is usual to avoid the necessity of making the pressure corrections by having a second apparatus in which the pure solvent is kept boiling, or by using Swietoslawski's differential ebulliometer. The latter contains two thermometer wells, one bathed with boiling liquid from the Cottrell lift and the other in the condensing vapour. The Beckmann thermometer can be quickly transferred from one well to the other to obtain the difference between the b.p. of the solution and that of the pure solvent. A simple and ingenious differential thermometer that registers the b.p. elevation directly was devised by Menzies and Wright.[3] Modern high-precision ebulliometers[4] employ a differential, multiple-junction thermocouple in conjunction with a sensitive galvanometer to measure the b.p. elevation. The apparatus is calibrated with a solute of known molecular weight.

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6D. DISTRIBUTION OF A SOLUTE BETWEEN IMMISCIBLE SOLVENTS

When a substance is "extracted" from aqueous solution by means of ether—a common operation in organic chemistry—the extraction is not complete, but the solute distributes itself between the two solvents according to its "solubility" in each.   Such solutions cannot both obey Raoult's Law, but as a first approximation, they generally follow Henry's Law, according to which the partial pressure (or activity) of the solute is proportional to its concentration (provided the solutions are very dilute).   The proportionality constants are different, however, for the two solvents.   It follows, therefore, that at a given temperature the solute distributes itself in a constant ratio between the two liquids.   This ratio, called the distribution (or partition) coefficient, is generally approximately independent of the total concentration (Nernst's Distribution Law).

Deviations from the law occur when the solute undergoes chemical changes in one of the phases and not in the other.   The law is then applicable to the concentration of any particular chemical species in the solutions, although not to the total concentration of the substance.   Measurements of the distribution can thus afford a method of studying such processes as association, dissociation, solvation, hydrolysis, complex formation and "salting-out".   Approximate values of the corresponding equilibrium constants may be obtained, but the method is limited quantitatively by the assumption that Henry's Law holds for the species concerned.   The following examples will serve to illustrate the method.   Since no special experimental technique is required, further examples will not be given here in detail.

(1) *Simple partition: iodine between water and carbon tetrachloride.*
   Here the molecular condition of the solute is the same (I_2) in both solvents and the distribution coefficient, k, is practically independent of concentration.

(2) *Complex formation: iodine between carbon tetrachloride and solutions of potassium iodide.*

The distribution ratio varies with concentration because in the aqueous phase the reaction $I_2 + KI \rightleftarrows KI_3$ occurs to some extent, the mass action constant being given by $K = \dfrac{[KI_3]}{[KI][I_2]}$.   Since KI and KI_3 are electrolytes and therefore insoluble in CCl_4, the only species

undergoing distribution is molecular I_2, which still follows its characteristic distribution coefficient, k. Hence, measurement of the concentration of I_2 in the CCl_4 layer, together with a knowledge of k, gives the *equilibrium concentration* of I_2 in the aqueous phase. This concentration is less than the total, titratable iodine present, as the rest is bound as KI_3. The equilibrium constant can therefore be calculated from such measurements.[1]

EXPERIMENT

Determine the equilibrium constant of the reaction $KI + I_2 = KI_3$ *by the distribution method.*

Practical details. One must first determine the distribution coefficient of iodine between water and a suitable non-miscible solvent, such as carbon tetrachloride or carbon disulphide. To do this, prepare a saturated solution of iodine in, say, carbon tetrachloride at the ordinary temperature, and shake up 20 ml of this solution with 200 ml of water in a stoppered bottle immersed in the water of a thermostat at 25°. After equilibrium has been attained, allow the bottle to stand in the thermostat for 20–30 minutes so as to secure complete separation of the two liquid layers. The concentration of iodine in the carbon tetrachloride and in the water is then determined by pipetting out a given volume of the solutions (say, 5 ml of the carbon tetrachloride solution and 50 or 100 ml of the aqueous solution), and titrating with $0.05N$ or $0.01N$ thiosulphate solution. (A small quantity of a concentrated solution of potassium iodide is added to the carbon tetrachloride solution in order to ensure complete extraction of the iodine, and the two layers should be well shaken during the titration.) The determination is repeated, using (a) 10 ml of saturated iodine solution, 10 ml of carbon tetrachloride, and 200 ml of water; (b) 15 ml of iodine solution, 5 ml of carbon tetrachloride, and 200 ml of water. The distribution coefficient is then obtained from the expression $k = \dfrac{\text{concentration in } CCl_4}{\text{concentration in } H_2O}$. Similar experiments are then carried out using, in place of water, a solution of potassium iodide of known concentration (say $0.1N$). The iodine in the two layers is accurately titrated by means of thiosulphate solution. The concentration of iodine in the two solvents is thereby known. From the concentration of iodine in carbon tetrachloride, the concentration of free iodine in the aqueous solution can be calculated from the distribution coefficient. The titration value of the iodide solution gives the total iodine, and the difference between this and the amount of free iodine gives the iodine combined with potassium iodide to form KI_3. The amount of iodide which has thus combined with iodine can be calculated, and if this amount of iodide is subtracted from the original amount of iodide present, the amount of uncombined iodide is obtained. In this way, the amounts of KI, I_2, and KI_3 in a given volume of solution can be obtained, and the concentrations calculated. If the equilibrium between KI, I_2 and KI_3 is produced in

accordance with the expression $KI + I_2 \rightleftarrows KI_3$, the equilibrium constant, according to the law of mass action, should be

$$K = \frac{[KI_3]}{[KI][I_2]}$$

where the square brackets indicate concentrations.

Other systems suitable for study by the distribution method:

Simple partition: succinic acid between ether and water.

Dimer formation of carboxylic acids: benzoic acid between water and benzene.

Electrolytic dissociation: monochloracetic acid between water and ether.

Hydrolysis of salts: aniline hydrochloride between water and benzene.

Complex formation: ammonia between chloroform and copper sulphate solutions.

"*Salting-out*" *and* "*salting-in*": benzoic acid between benzene and aqueous solutions of various electrolytes; tetraethyl-ammonium iodide salts "in".[2]

Measurement of activity coefficients: hydrochloric acid between water and benzene, and salt solutions and benzene.

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6E. HOMOGENEOUS EQUILIBRIA IN SOLUTION

Theory.   The reversible reaction $KI(aq) + I_2(aq) = KI_3(aq)$ discussed in the previous section is an example of a large class of reactions which exhibit homogeneous equilibria in solution.   The state of equilibrium is governed rigorously by a thermodynamic mass action product: for example,

$$K_{Th} = a_{KI_3}/a_{KI} \times a_{I_2}$$

where the a terms are thermodynamic *activities*.

In the classical treatment of equilibria by Guldberg and Waage, it was assumed that the "active mass" of a substance in solution could be taken as equal to its *concentration*.   This is now known to be only approximately correct.   Nevertheless, in many cases an equilibrium constant formulated in terms of concentrations is found to be approximately constant for a series of solutions of different concentration.   Strictly, the concentrations should be multiplied by *activity coefficients* (cf. p. 241) but these may be nearly constant, or may partially cancel, as in the KI_3 equilibrium.

Many methods have been employed for arriving at the composition of equilibrium solutions, and hence determining equilibrium constants.   A number of examples will be found in different places in the present book, and only one other need be given here, namely,

a case in which the amount of product formed in solution can be determined by optical measurements of the intensity of colour of the solution.

Complex-formation between salicylic acid and ferric salts. Many phenolic compounds give strongly coloured products when treated with solutions of ferric salts. The coloured substance appears to be a weak "complex" which is in equilibrium with the reactants.

Foley and Anderson [1] studied the stoichiometry of such complexes by measuring the intensity of colour produced with different proportions of the reactants. A theory due to Job [2] was employed which indicates that when *equimolar* solutions of two reactants are mixed in various proportions, the maximum amount of equilibrium product is formed when the proportions of reactants employed correspond to the empirical formula of the product. For example, if the stoichiometry of the reaction can be represented by $aA + bB \rightleftharpoons A_aB_b$, then the greatest amount of A_aB_b is present if a parts of a solution of A are mixed with b parts of an (equimolar) solution of B.

EXPERIMENT

Determine the empirical formula and approximate standard free energy of formation of the complex between salicylic acid and ferric ions.

Procedure. The optimum pH for the complex is about 2·6–2·8. This may be obtained sufficiently nearly by working throughout with very dilute solutions of the substances in approx. $N/500$ HCl; prepare 2 litres of this acid.

Prepare 500 ml of a $1·00 \times 10^{-3} M$ solution of salicylic acid in $N/500$ HCl, and 500 ml of a solution of ferric ammonium alum, $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, in $N/500$ HCl, the latter to contain $1·00 \times 10^{-3}$ *g ions* of Fe^{+++} per litre. This solution hydrolyzes on standing and must therefore be used at once for preparing the equilibrium mixtures.

By means of two burettes, prepare a series of mixtures of the salicylic acid and ferric salt in different proportions, ranging from 1 : 10 to 10 : 1.

Determine the intensity of the colour (% absorption) of the mixtures by means of a photo-electric absorptiometer (pp. 167–9), using a filter of complementary colour to that of the solution—i.e. the filter which shows the smallest percent transmission for the solution as compared with pure water as 100.

In addition, take 10 ml each of $1·00 \times 10^{-3}$, $0·75 \times 10^{-3}$, $0·50 \times 10^{-3}$, $0·25 \times 10^{-3}$, and $0·1 \times 10^{-3}$ M ferric solution and add *excess* solid salicylic acid in order to convert the ferric salt wholly into the complex form. Determine the percent absorption of these solutions.

Treatment of results. Plot a graph of percent absorption against molar

composition of the mixtures made from equimolar solutions. The maximum in the curve gives the empirical formula of the complex.

Calculate the *optical density* (p. 160) of the five solutions used in the second part of the experiment, and plot the resulting values against concentration of ferric ion. If Beer's Law is obeyed, the graph should be a straight line through the origin, and the slope of the line gives the extinction coefficient of the complex. This graph can now be used to calculate the concentration of the complex present in the different reaction mixtures. Since the formula of the complex has been found, it is now possible to calculate also, by difference, the concentration of *uncombined* salicylic acid and Fe^{+++} present in the various mixtures, and hence to evaluate the classical equilibrium constant, K_c, for the reaction.

The standard free energy for the formation of the complex is given by

$$\Delta G^\circ = -RT \log_e K_c$$

and it corresponds to the free energy change accompanying the formation of a $1M$ solution of the complex from $1M$ solutions of salicylic acid and Fe^{+++} salt.

In considering the probable electronic structure of the coloured complex, one must take the following points into consideration. (1) The profound change of colour shows that the electronic condition of the Fe^{+++} ion has been changed; the colour of the ferric ion is probably connected with an internal electronic transition involving the incomplete $3d$ shell. (2) At pH $2 \cdot 6$–$2 \cdot 8$ both the phenolic –OH group and the carboxylic –COOH will be undissociated. (3) No similar coloured complex is formed by ferric ions with either *meta*- or *para*hydroxybenzoic acid.

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PHASE EQUILIBRIA

The condition for equilibrium in heterogeneous systems is given by the phase rule: $F = C+2-P$, where F is the number of degrees of freedom, C the number of components, and P the number of phases present. For example, when $P = C+2$, the system has no degrees of freedom; the temperature and pressure under which it can exist are perfectly definite. If one of the variables, temperature or pressure, is fixed, then equilibrium will be definitely fixed when $P = C+1$. Thus, if the pressure is fixed (say, atmospheric) then equilibrium between a solid and a liquid phase of a single substance will be defined by a definite temperature, namely, the m.p.

Owing to the importance of heterogeneous equilibria, a number of different cases will be studied. The equilibrium between a pure liquid and its vapour, and the f.p. and the b.p. of dilute solutions have already been considered. (Chs. 5, 6.)

7A. VAPOUR PRESSURE OF SALT HYDRATES

A salt hydrate is a two-component system. When dehydration occurs a second solid phase, anhydrous salt or lower hydrate, is formed, and the system then consists of three phases—two solid phases and one vapour phase. The system is therefore univariant, and the vapour pressure will vary with the temperature. If, however, the temperature is kept constant the vapour pressure will be constant. This vapour pressure may be measured, for example, by the dew-point method.[1]

EXPERIMENT

Determine the vapour pressure of sodium sulphate decahydrate.

The apparatus (Fig. 7.1) consists of a wide-mouthed bottle, *B*, which is closed by a rubber stopper. Through this stopper pass a closed tube of bright silver, *A*, and the glass tube *C*, which is furnished with a stopcock. The mouth of the silver tube also is closed by a rubber stopper, through which pass a thermometer, *T*, graduated in tenths of a degree, and two narrow glass tubes. One of these reaches nearly to the bottom of the silver tube, the other just passes through the stopper. Before being used for an experiment, the silver tube, which must be brightly polished, is dipped into boiling

distilled water. In this way, a boundary line is produced which becomes visible only when dew is deposited on the tube and which renders the deposit more easily detectable.

A quantity (10–15 g) of roughly powdered sodium sulphate decahydrate is placed at the bottom of the dry bottle, *B*, and the rubber stopper, carrying its silver and glass tubes, is placed firmly in position. A quantity of ether is poured into the silver tube which is then stoppered, and the bottle is supported in a beaker of water, the temperature of which is maintained constant at, say, 20° or 25°. Tube *C* is connected with a water pump and the bottle is partially exhausted. The stopcock on *C* is then closed.

When the bottle and its contents have taken the temperature of the bath, air is blown through the ether by means of a rubber bulb tube. The ether is thereby caused to evaporate rapidly, and the temperature of the silver tube falls. Stop evaporating the ether, allow the temperature of the silver tube to rise, and note the point at which the film of dew disappears. Several readings of the appearance and disappearance of the dew should be made, and the mean taken. This is the dew-point. From the tables of vapour pressure of water, the pressure corresponding to the dew-point is obtained, and this gives the vapour pressure of the system $Na_2SO_4.10H_2O$–Na_2SO_4–$H_2O(vapour)$ at the temperature of the bath.

FIG. 7.1. Determination of aqueous vapour pressure by the dew-point method.

In the same way, one may determine the dissociation pressures of $CuSO_4.5H_2O$ and of $MgSO_4.7H_2O$ at, say, 20–30°. The method may also be used to determine the vapour pressure of aqueous solutions. McBain and Salmon[2] refined the technique so that the dew-point could be determined to $\pm 0.01°C$.

The vapour pressure of a hydrate may also be determined by finding the concentration of a solution of sulphuric acid (or potassium chloride, etc.) with which the hydrate is in equilibrium.[3] The vapour pressure of the solution can be obtained from tables. This is the principle of the isopiestic method for measuring the v.p. of solutions.[4]

Salts in contact with their saturated solutions provide convenient means of controlling the *relative humidity* in a closed vessel. A list of suitable salts is given in the Appendix, Table A7.

BIBLIOGRAPHY 7A: Vapour pressure of salt hydrates

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7B. DETERMINATION OF SOLUBILITY

Gases are miscible in all proportions, but other phases more often show only partial miscibility.   One often needs to know the solubility of a gas in a liquid or solid, of a liquid in another liquid, or of a solid in a liquid.   Solutions of solids in solids are important among metals.

1. Solubility of a gas in a liquid.   In the equilibrium between a gas

and a liquid, only two phases are present— the system, therefore, is bivariant.   In order that the condition of equilibrium may be defined, it is necessary to fix two of the independent variables, temperature and pressure.

The solubility of a gas in a liquid can readily be determined by means of the apparatus shown in Fig. 7.2, except in those cases where the gas is very soluble (ammonia, hydrogen chloride, etc.).[1]   The apparatus consists of a gas-measuring burette, A, connected with a levelling tube, B.   The burette is furnished with a 3-way tap, a, which connects on the one side with the gas supply, and on the other, with a tube leading to the "absorption pipette" C, also furnished with the 3-way tap b, and an ordinary tap, c.   The gas burette and absorption pipette are connected by a length of thick-walled rubber tubing of narrow bore.
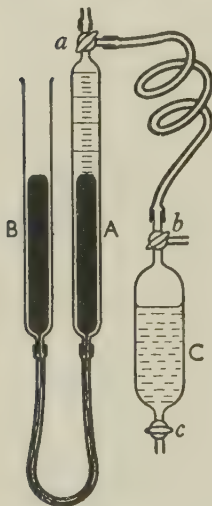
Fig. 7.2. Determination of the solubility of a gas in a liquid.

Before carrying out a determination, the volume of the absorption pipette between the two taps must be determined by means of water or mercury.   For the solubility of gases such as carbon dioxide, the pipette may suitably have a volume of about 100 ml.   For less soluble gases the volume should be greater.

The solvent to be used for the absorption of the gas must first be freed from air; this is best done by boiling the liquid for some time in a flask with reflux condenser attached.   The flask is best fitted up as shown in Fig. 7.3.   The side tube, a, of the round-bottomed distilling flask is connected with a condenser by means of a piece of rubber tubing having a screw clip, c.   Through a rubber stopper in

the neck of the flask passes a glass tube, *b*, which reaches nearly to the bottom of the flask. The other end of the tube is closed by rubber tubing and a clip.

While the liquid is being boiled, the clip on the tube *b* is closed while there is free connection with the condenser. After the liquid has been boiled for 10–15 minutes, the clip *c* is closed and the flame at the same time removed. After the liquid has cooled down to the ordinary temperature the flask is inverted and connected, by means of the side tube, with the lower outlet tube of the absorption pipette. The absorption pipette is exhausted by means of a pump attached to the tube *b* of the absorption pipette and the taps then closed. The clip on the tube *b* of the distillation flask is now opened in order to bring the interior of the flask to atmospheric pressure, and then, *as soon as possible*, the clip *c* is opened and also the lower tap of the absorption pipette. The solvent is then drawn into the pipette from the bottom of the liquid in the boiling flask, to which the air admitted into the flask will not have had time to diffuse.

FIG. 7.3. Preparation of air-free liquid.

EXPERIMENT

Determine the solubility of carbon dioxide in water at 25°.

Procedure. The apparatus having been fitted together, the absorption pipette, filled with air-free water, is placed in a thermostat at 25°. The mercury in the measuring burette is raised until it completely fills the burette, and a current of moist carbon dioxide from a Kipp apparatus is allowed to pass through the connecting tube and to escape into the air through the 3-way tap on the absorption pipette. When all the air has been swept out, the tap *a* is turned and the burette filled with carbon dioxide. After adjusting the levels of the mercury, the volume is read off. A slight increase of pressure is now established in the burette and the tap *a* turned so as to make connection between the burette and the pipette. The tap *c* of the pipette is opened and then the tap *b*, and a certain amount (say (20–30 ml) of water allowed to run out into a flask. The weight of water run out is then determined. The volume of the water in the pipette, and also the air-space, can thus be calculated, since the total volume of the pipette is known.

The pipette is replaced in the thermostat and is shaken carefully from time to time, the gas in the burette being always in communication with the pipette. As absorption of the gas proceeds,
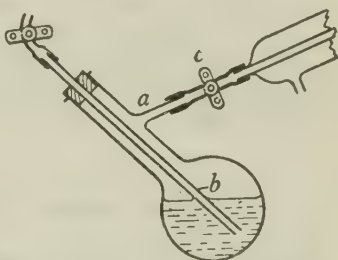
the levelling tube of the burette is raised so as always to maintain the gas at atmospheric pressure. When the absorption of gas ceases, the volume left in the burette is read off.

Calculation. If the solubility S of a gas in a liquid is defined by the ratio of the volume of gas absorbed to that of the absorbing liquid, one obtains

$$S = \frac{1}{V_2}\left[v_1\left(\frac{P_1-p_1}{P_2-p_2}\cdot\frac{T_3}{T_1}\right) - v_2\left(\frac{P_2-p_1}{P_2-p_2}\cdot\frac{T_3}{T_2}\right) - V_1\right]$$

where v_1 is the initial and v_2 the final volume of gas in the burette; P_1 is the initial and P_2 the final barometric pressure; p_1 is the partial pressure of the water vapour at the initial absolute temperature of the burette and p_2 the partial pressure at the temperature of the thermostat; T_1 is the initial and T_2 the final absolute temperature of the burette, and T_3 the absolute temperature of the thermostat; V_1 is the volume of the gas space and V_2 the volume of the liquid in the pipette.

Instead of filling the burette with moist gas, it is better first to dry the gas by means of Anhydrone. When dry gas is employed in the burette, a short tube of Anhydrone should be inserted between the connecting tube and the absorption pipette; also, the 3-way tap of the absorption pipette should be kept closed except when it is necessary to allow gas to pass from the burette to the pipette. Under these conditions, the solubility is given by the expression

$$S = \frac{1}{V_2}\left\{\left[(v_1-v_2)\frac{P}{P-p_2}\cdot\frac{T_3}{T_1}\right] - V_1\right\}$$

The barometric pressure P is supposed not to change during the experiment.

The solubility S of carbon dioxide in water at 25° C is equal to 0·82.

2. Solubility of a liquid in a liquid. When ether is shaken with water a definite amount of the ether dissolves in the water, and similarly a definite amount of water dissolves in the ether. One thus obtains two liquid solutions the composition of which depends on the temperature. At each temperature, therefore, there will be two solubility values, one representing the solubility of ether in water, and the other the solubility of water in ether.

When the liquids are such that the amount of one of them can conveniently be determined by analysis, the mutual solubility curve is easily determined. The two liquids are shaken together in a stoppered bottle immersed in a thermostat, and the bottle is then allowed to remain undisturbed until the two liquid layers have separated. A quantity of each layer is then pipetted out, weighed, and the amount of one of the components determined by analysis. Such a method, for example, can be employed in the case of aniline and water, the aniline being titrated by means of a solution of potassium bromate and bromide of known concentration. Similarly, also, with phenol and water. Physical methods of analysis can often be used.

In many cases, however, the analytical method is not convenient and it is therefore necessary to employ the synthetic method. Weighed amounts of the two components are placed in a small glass tube, and the end of the tube then drawn out and sealed off. So long as two liquid layers are present, a turbid liquid is formed on shaking the tube, but at the temperature at which one of the layers just disappears, this turbidity also disappears, and a single homogeneous solution is now obtained which represents a saturated solution of one of the liquids in the other. Since the composition of the solution and the temperature at which the turbidity disappears are known, a point is obtained on the mutual solubility curve of the two liquids. By varying the initial amounts of the two liquids, the complete solubility curve can be obtained.

EXPERIMENT

Determine the mutual solubility curve of phenol and water.

A number of tubes are prepared about 10 cm long and 1 cm wide, and with a constriction near the open end; alternatively, tubes fitted with a stopper which can be held in place by means of two springs may be used. Into these tubes are introduced, by means of narrow-stemmed pipettes or funnels, different relative amounts of phenol and water, the weights of which are determined. The tubes are placed in holders formed, for example, of stout copper wire, and are immersed in turn in a large beaker full of water, in which also is a thermometer graduated in tenths of a degree. The water is warmed and, during this time, the tube with the two liquids is shaken at frequent intervals. At first the temperature may be allowed to rise rapidly until the turbidity shows signs of disappearing, after which the temperature must be raised only slowly, and the tube must be shaken frequently. At the moment when the turbidity disappears on shaking, the temperature is read. The temperature of the bath is now allowed to fall very slowly, and the point is noted at which the turbidity just begins to appear once more. The experiment is repeated once or twice, and the mean of the temperatures at which the turbidity disappears on heating and reappears on cooling is taken as the temperature at which phenol and water, in the particular proportions taken, become completely miscible. In a similar manner the temperatures are obtained for other mixtures of phenol and water. The results are then plotted with percentage amounts of one component as abscissae against temperatures at which homogeneity occurs as ordinates, and a smooth curve is drawn through these points. The maximum temperature point on the curve is known as the critical solution temperature.

This critical solution temperature is very greatly influenced by the

presence of impurities, and this fact may be made use of for the purpose of detecting the presence of impurities, or, in other words, as a criterion of purity.

Additional experiments may be carried out with the following pairs of liquids: iso-butyric acid and water, hexane and methyl alcohol, carbon disulphide and methyl alcohol, acetylacetone and water.

The system *n*-butyl cellosolve (i.e ethylene glycol monobutyl ether)+ water is unusual in that these liquids are miscible in all proportions at room temperature, but separate into two phases in the region 50–130° C. Above 130° C they are once more completely miscible. The miscibility gap is therefore a closed loop. The phenomenon of "salting-out"[2] is readily demonstrated with this system.

Three-component liquid systems. The mutual solubility of a pair of partially miscible liquids may be markedly altered by the addition of a third component. In general, when the third component is soluble in only one of the other two components, the mutual solubility of the two liquids is diminished; but when the third component dissolves readily in each of the other two components the mutual solubility of the latter is increased. This behaviour is illustrated by the system chloroform–water–acetic acid. When acetic acid is added to a heterogeneous mixture of chloroform and water at a definite temperature, the mutual solubility of these two liquids is increased, and a point is reached at which the mixture becomes homogeneous. The amount of acetic acid which must be added to bring about homogeneity at the given temperature will depend on the relative proportions of chloroform and water in the original mixture. Similarly, when water is added to a homogeneous mixture of chloroform and acetic acid (two completely miscible liquids), a heterogeneous mixture (two liquid solutions) is formed when a certain amount of water, depending on the initial composition of the mixture, has been added.

EXPERIMENT

Determine the limit of homogeneous phase in the system chloroform– acetic acid–water.

Mixtures of chloroform and acetic acid of varying composition are made up in a set of five stoppered bottles of 70–80 ml capacity. These mixtures may suitably contain 10, 20, 40, 60 and 80% of chloroform by weight respectively. Since the densities of chloroform and acetic acid are 1·50 and 1·05 respectively, the mixtures may be prepared by running into the bottles from burettes the following volumes of chloroform and acetic acid:

| chloroform (ml) | 1·67 | 3·33 | 6·66 | 9·99 | 13·32 |
| acetic acid (ml) | 21·43 | 19·05 | 14·30 | 9·53 | 4·77 |

The bottles containing the solutions are placed in a thermostat at 18° and after they have taken the temperature of the bath water is run, in small quantities at a time, into each of the bottles in turn; and after each addition the bottle is well shaken. Addition of water is continued until, on shaking, a turbidity appears. The final additions of water should be made drop by drop, care being taken not to add too much water, especially in the case of the solutions richest in chloroform. From the amount of the water added and the initial amounts of chloroform and acetic acid, the percentage composition of the mixture when turbidity makes its appearance is calculated, and the results are plotted in a triangular diagram. The points obtained are joined by a smooth curve, which may be completed by means of the following data: A saturated solution of water in chloroform contains 99% of chloroform, while the conjugate saturated solution of chloroform in water contains 0·8% of chloroform.

The triangular diagram. A triangular diagram usually consists of an equilateral triangle. The length of the side is taken as unity or 100, and represents, therefore, the sum of the fractional or percentage amounts of the three components; each corner of the triangle represents 100% of one of the components (Fig. 7.4). In plotting the composition of a ternary mixture, two points are marked on one side of the triangle, representing the

Fig. 7.4. Representation of the composition of a ternary mixture by means of triangular co-ordinates.

percentage amounts of two components, and from these points lines are drawn parallel to the other two sides of the triangle. The point of intersection gives the composition of the ternary mixture. Printed triangular co-ordinate graph paper is obtainable

Thus, to represent the composition, 15·1% of chloroform, 50·2% of acetic acid and 34·7% of water, the side of the triangle for chloroform and acetic acid (Fig. 7.4) is marked at the two points representing 15·1% of chloroform and 50·2% of acetic acid, and lines are drawn from these points parallel to the sides of the triangle. The point of intersection x, represents the composition of the above ternary mixture.

Results. The curve obtained by joining the experimentally determined points forms the boundary between homogeneous and heterogeneous mixtures. A mixture of chloroform, acetic acid and water represented by any point *outside* the curve, towards the acetic acid corner of the triangle, will form only one homogeneous solution, while any mixture represented by a point *within* the curve will separate into two layers.

If it is required to draw *tie-lines* across the miscibility gap to indicate

conjugate solutions, pairs of mutually saturated solutions must be analyzed. Since the binodal curve has been determined in the above experiment it will suffice to analyze for acetic acid only.

Additional experiments.   The system benzene–acetic acid–water may be studied at 20° in the manner described above.   Further, the boundary curve for chloroform, acetic acid and water may be determined at a series of temperatures, and the curves plotted on the same triangular diagram. The construction of a three-dimensional model would also be instructive.

It will also be of interest to study, between 50° and 100°, the system water–phenol–aniline and the system water–ether–succinic nitrile at 60°.

3. Solubility of solids in liquids.   When a solid is brought into contact with a liquid in which it can dissolve, a certain amount of it passes into solution, until the solution is *saturated*.   In all determinations of the solubility it is necessary, not only to determine the amount of dissolved substance in the solution, but also to ascertain the nature of the solid phase which is in equilibrium with the solution.

The amount of substance dissolved depends, also, on the temperature; the solubility of a substance, or the number of grams of substance dissolved by a given weight of the solvent, may either increase or decrease with rise of temperature, according to whether the dissolution is endothermic or exothermic, respectively.   In all cases, however, the solubility curve of any substance is continuous so long as the solid substance in contact with the solution remains unchanged. If, however, a change in the solid phase occurs, the solubility curve will show a "break" or discontinuous change in direction.

It takes an appreciable time to saturate a liquid with a solid. The length of time required not only varies with the state of subdivision of the solid and the efficiency of the shaking or stirring, but is also dependent on the nature of the substance.   In all cases, therefore, care must be taken that sufficient time is allowed for equilibrium to be established, more especially when changes in the solid may occur.

In cases where the solubility increases with rise of temperature, the time required for the attainment of equilibrium can generally be shortened by preparing a saturated solution at a higher temperature and allowing it to cool to the desired temperature in contact with the solid phase.   Particular care, however, must be exercised in cases where the solid phase itself undergoes change with the temperature.

Determination of the solubility.   The production of a saturated solution can be carried out very simply in the apparatus shown in Fig. 7.5.   It consists of a boiling-tube, *a*, in which the solid and solvent are vigorously stirred by means of the glass screw stirrer

shown at *b*. The stem of the latter passes through a glass tube, inserted in the rubber stopper by which the solubility tube is closed. The tube should be chosen of such a size that the stem of the stirrer just passes through. The bearing is well lubricated by means of vaseline. The boiling-tube must be immersed in a thermostat.

The progress of solution towards saturation can be tested by withdrawing some of the solution from time to time, and determining the amount of dissolved substance, e.g. by means of refractive index measurement (p. 178). This requires to be done once only, the solution in other experiments being then well stirred for a period somewhat longer than that required for complete saturation.

When saturation has been effected, the solution must be analyzed. The stirrer is removed from the tube, and the latter closed with an unbored cork, the solubility tube being meanwhile kept in the thermostat. After the solid has subsided, a known volume of the solution is transferred to a tared weighing bottle by means of a pipette to the end of which is attached by rubber tubing a short glass tube filled with cotton-wool to act as a filter. The solution is then weighed. The density of the solution can in this way be determined. The amount of solid in solution is determined in an appropriate manner, most simply (if allowable) by evaporation on the water-bath, and drying, if necessary, at a slightly higher temperature, or by gravimetric or volumetric analysis.

FIG. 7.5. Apparatus for saturating a liquid with a solid.

When the temperature of experiment is fairly high, it may be necessary to warm the pipette first before withdrawing the solution, otherwise solid may separate out in the pipette.

EXPERIMENT

Determine the solubility of potassium chloride from 10° to 50° C.

Fit up a thermostat and regulate the temperature so as to be at about 5–8°, the variations of temperature being not greater than 0·1°. In the solubility tube (Fig. 7.5) place a quantity of *finely powdered* potassium chloride and water, and after fitting a stirrer, place the tube in the thermostat so that it is immersed up to the level of the cork. The solid and solution should now be stirred for 2–3 hours, and a quantity of the solution removed as described above, weighed, and evaporated to dryness, or analyzed by titration. To the solution in the tube add a further quantity of *finely powdered*

potassium chloride, and allow the stirring to continue for another period of 2–3 hours. Again determine the composition of the solution. If this agrees with the former determination, it shows that saturation was complete in the first period of 2–3 hours; but if the amount of dissolved solid is greater in the second case, the stirring must be continued for some time longer, with addition, if necessary, of more potassium chloride until the concentration of the solution becomes constant. This gives the solubility at the particular temperature of the experiment, and should be checked by a second, independent determination. Express the solubility as grams of salt to 100 grams of water.

Having determined the solubility at a temperature between 5° and 8°, raise the temperature of the thermostat by 5° or 10° and make another determination of the solubility at this higher temperature. Make further determinations at intervals of about 10° up to 50–55°. Instead of making two determinations at each temperature, as mentioned above, the first series of determinations can be checked by approaching saturation from the side of supersaturation, i.e. by allowing the solution to cool down from a higher temperature *while in contact with the solid*. The solid phase must be present, and the solutions should be stirred.

Results. The results are plotted in rectangular co-ordinates, the temperatures being plotted as abscissae, and the solubility (grams of salt to 100 grams of water) as ordinates. Draw a smooth curve through the points so obtained, and from the curve read off the solubility at every five degrees.

When the van't Hoff reaction isochore is applied to solubilities, one obtains the expression $\dfrac{\mathrm{d}\log_e S}{\mathrm{d}T} = \dfrac{Q}{RT^2}$ where S is the solubility in moles per litre and Q the heat of solution. Assuming (what is generally not quite true) that Q is independent of the temperature, this expression yields, on integration, $\log_{10} S_2 - \log_{10} S_1 = \dfrac{Q(T_2 - T_1)}{2 \cdot 303 \times 1 \cdot 99 \times T_2 \times T_1}$.

The value of Q calculated from the solubility may also be compared with the (different) heat of solution, determined calorimetrically (p. 190–1).

Additional exercise. The solubility of benzoic acid may also be determined at temperatures between 20° and 60°. The amount of benzoic acid in a definite volume and weight of saturated solution can be determined by titration with $0 \cdot 25N$-NaOH, using phenol-phthalein as indicator, the solution of benzoic acid being first diluted as may be necessary. (Solubility at 20° = 0·290, and at 60°, 1·155 g per 100 g of water.)

In the case of potassium chloride and benzoic acid the solid phase remains unchanged throughout the whole range of temperature. A case may now be studied where the solid phase undergoes change.

EXPERIMENT

Determine the solubility of sodium sulphate from 10° to 50°.

Details. The determinations of the solubility are carried out exactly as described above. Between 28° and 35°, determinations should be made at every two degrees. The results are then plotted graphically as before, the solubility being calculated in grams of *anhydrous* salt to 100 g of water.

At the temperature of 30°, and also at the temperature of about 35°, the excess of solid in contact with the solution should be rapidly separated by filtration with the aid of a water-pump, using for the filtration merely a loose plug of cotton-wool in the stem of the funnel, or a sintered glass filter may be used. The solid is then rapidly pressed between filter-paper, and the amount of water of crystallization determined in the ordinary way. The solubility curves obtained from the above determinations should be produced so as to cut each other. The point of intersection gives the *transition point* of the phase reaction

$$Na_2SO_4.10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$$
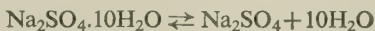
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7C. TRANSITION POINTS

It is well known that there are many substances which are capable of existing in more than one crystalline form, e.g. sulphur. In general, these different polymorphous forms are not equally stable at a given temperature. Thus, at the ordinary temperatures, rhombic sulphur is the more stable form, and monoclinic sulphur, if kept sufficiently long, will change spontaneously into rhombic. If, however, the temperature is raised to, say, 100–110°, it is found that the monoclinic crystals can be kept indefinitely without undergoing change, while the rhombic crystals pass into monoclinic. At this temperature, therefore, the monoclinic is the more stable form.

At a temperature of about 96°, it is found that the two forms are equally stable, and that neither form changes into the other on keeping. This temperature is known as the *transition temperature*, or transition point. Graphs of the molar *free energies* of the two forms cross at this temperature, the upper curve being that of the metastable form at other temperatures.

Not only are transition points found with polymorphous substances, but they are found, in general, also with salt hydrates. When a salt combines with water to form one or more different

hydrates, it is found that under given conditions of temperature, etc., only one of the hydrates, or it may be the anhydrous salt, is stable. Thus, when sodium sulphate decahydrate is heated above 33°, it decomposes into anhydrous sodium sulphate and a saturated solution of this salt. On the other hand, on allowing a saturated solution of sodium sulphate to cool down in presence of anhydrous sodium sulphate, it is found that when the solution is cooled below about 33° the anhydrous salt takes up water and forms crystals of the decahydrate. The temperature of (approximately) 33° therefore constitutes a transition point or inversion point for the change $Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$. Similar relationships are, in general, found with other salt hydrates, e.g. sodium carbonate hydrates.

Determination of the transition point. Various methods have been employed for the determination of the transition point of a polymorphous solid or of a salt hydrate. The different methods, however, are not equally suitable in every case; nor are the values obtained by the different methods always identical. It is well, therefore, to determine the transition point by different methods. The more important of these are: solubility, thermometric, dilatometric, and tensimetric methods.

1. *Solubility method.* This has already been studied in the preceding section.

2. *Thermometric method.* The thermometric method depends on the fact that change from one form to another on passing through the transition point is accompanied by a heat effect—absorption or evolution of heat. Thus, when $Na_2SO_4.10H_2O$ breaks up into Na_2SO_4 plus solution, heat is absorbed, while the reverse change is accompanied by evolution of heat.

EXPERIMENT

Determine the transition point of sodium sulphate by the thermometric method.

A quantity (30 to 50 g) of recrystallized sodium sulphate decahydrate is placed in a thin glass tube so as entirely to surround the bulb of a thermometer, graduated in tenths of a degree. The tube is placed in a large beaker of water, the temperature of which can be very slowly raised by means of a small flame, and be kept uniform by means of a stirrer. The temperature of the bath is raised to about 32°, at which it may be kept for several minutes, and then very gradually raised until the Glauber's salt becomes partially liquid. The temperature of the bath is then kept constant. The partially liquefied mass in the tube is now well stirred by means of a ring stirrer of glass or platinum, as in carrying out a f.p. determina-

tion with the Beckmann apparatus (p. 107), and the temperature of
the mass read from time to time. Meanwhile the temperature
of the bath may be allowed to rise very slowly ($1°$ in 5 minutes), and
the temperature of the partially liquefied mass should be read
every minute. After the temperature of the bath and of the partially
liquefied mass has risen to about $34°$, allow the temperature to fall
slowly. Meanwhile stir the sodium sulphate and solution well, and
read the temperature every minute.

The temperature readings for the mixture in the tube are plotted
against the time, and in this way two curves will be obtained, one
for rising and the other for falling temperature, each showing an
approximately horizontal portion. Owing to suspended
transformation, these two horizontal portions may not
coincide.

Repeat the experiment, but allow the temperature of
the bath to rise more slowly between $32°$ and $33°$. Again
read the temperature on the thermometer in the tube every
minute, and plot the results as before.

Similar determinations may also be carried out with the
salts given in Table A2 of the Appendix.

3. *Dilatometric method.* Since, in the majority of cases,
transformation at the transition point is accompanied by
an appreciable change of volume, it is only necessary to
ascertain the temperature at which this change occurs in
order to determine the transition point. For this pur-
pose the dilatometer is employed, an apparatus which
consists of a bulb with capillary tube attached, and which
constitutes a sort of large thermometer (Fig. 7.6). Some
of the substance to be examined is passed into the bulb *A*
through the tube *B*, which is then sealed off or closed by a
ground glass stopper. The rest of the bulb and a small
portion of the capillary tube are then filled with some

FIG. 7.6.
Dilato-
meter.

liquid which is without chemical action on the substance under
investigation. A liquid, however, may be employed which dissolves
the substance slightly.

In using the dilatometer, two methods of procedure may be
followed. According to the first method, the dilatometer containing
the form stable at lower temperatures is placed in a thermostat and
maintained at a constant temperature until it has taken the tempera-
ture of the bath. The height of the meniscus is then read on a
millimeter scale attached to the capillary. The temperature of the
thermostat is slowly raised, and the height of the meniscus at each
degree of temperature noted. If no change takes place in the solid,
the expansion will be practically uniform, or the rise in the level of

the meniscus per degree of temperature will be practically the same at the different temperatures, as represented by the line *AB* in Fig. 7.7. On passing through the transition point, however, there will be a more or less sudden increase in the rise of the meniscus per degree of temperature (line *BC*), if the change in the system is accompanied by increase of volume. Thereafter, the expansion will again become uniform (*CD*). Similarly, on cooling, contraction will at first be uniform, and then at the transition point there will be a large diminution of volume (*DE*, *EF*).

If the transformation occurred immediately the transition point was reached, the sudden expansion and contraction would take place at the same temperature. There is, however, always a certain time lag, so that, with rising temperature, the relatively large expansion does not take place until a temperature somewhat higher than

the transition point, and with falling temperature, the contraction occurs at a temperature somewhat below the transition point (e.g. *BC* and *EF*). The amount of lag will vary from case to case and will depend on the rapidity with which the temperature is raised and the velocity with which the system changes. After the transition point has been ascertained approximately in this way, the determination is made with greater care by allowing the temperature in the neighbourhood of the transition point to alter more slowly. In this way the amount of lag is diminished.

FIG. 7.7. Typical dilatometric records for heating and cooling a solid through its transition temperature.

Another method of using the dilatometer depends on the fact that while above or below the transition point transformation of one form into the other can take place, at the transition point the two forms undergo no change. The bulb of the dilatometer is charged, therefore, with a mixture of the stable and unstable forms and a suitable measuring liquid, and is then immersed in a bath at constant temperature. After the temperature of the bath has been acquired readings of the height of the meniscus are made from time to time to ascertain whether expansion or contraction occurs. If expansion is found, the temperature of the thermostat is altered until a point is reached at which a gradual contraction takes place. The transition point must then lie between these two temperatures; and by repeating the determinations it will be possible to reduce the difference between the temperatures at which expansion and contraction take place, to, say, 1°, and to fix the temperature of the transition point, therefore, to within half a degree.

EXPERIMENT

Determine the transition point for Glauber's salt and anhydrous sodium sulphate.

Procedure. Invert the dilatometer (Fig. 7.6), and drop into the bulb a small glass bead with stalk, so as to close the end of the capillary tube, and so prevent it being blocked by solid material. Then introduce a quantity of powdered Glauber's salt until the bulb is half or three-quarters full, and seal the end of the tube *B*. The dilatometer must now be filled with some measuring liquid, e.g. petroleum or xylene. This is best done by attaching an adapter to the end of the capillary tube by means of a rubber stopper. A quantity of petroleum is introduced into the wider portion of this tube, and the dilatometer then exhausted by means of a water-pump. On now allowing air to enter, petroleum is driven down into the bulb. The operation is repeated until all the air is withdrawn from the dilatometer and replaced by petroleum. Tap the tube so as to displace any adhering air-bubbles. The excess of petroleum is then removed from the capillary by means of a long, finely drawn capillary tube, so that when the dilatometer is placed in the thermostat, the petroleum meniscus remains on the scale.

Immerse the bulb of the dilatometer completely in the water of a thermostat, the initial temperature of which may be 25–26°. After about 5 or 10 minutes, read the level of the petroleum, and then slowly raise the temperature, 1° in 5 to 10 minutes, and at each degree again read the level of the meniscus in the capillary. At 32° to 33° it should be found that the rise of the meniscus per degree of temperature is relatively very large; and that as the temperature is raised above 33° the rise per degree becomes less again and nearly uniform. This shows that the transition point is between 32° and 33°. Carry out the same series of observations in the reverse order, allowing the temperature to fall from about 35° or 36° to about 28°. Then make a more accurate determination by allowing the temperature to alter very slowly from 31° to 34°.

4. *Vapour pressure method.* When the systems undergoing change at the transition point possess a measurable vapour pressure, e.g. salt hydrates, measurements of the latter may be used to determine the transition point. This depends on the fact that at the transition point the vapour pressure of the two systems becomes equal. A differential manometer is generally used.

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7D. FREEZING POINTS OF BINARY MIXTURES

When a homogeneous binary liquid mixture is cooled, a solid eventually separates, but its composition depends entirely on the nature of the substances concerned. If the two components are chemically dissimilar but form no compound, then each lowers the f.p. of the other; they crystallize out separately, and a *eutectic* system

is obtained, having a minimum f.p.   If, on the other hand, a stable compound (congruently melting) is formed, then the f.p. curve shows a maximum together with two eutectic minima.   In some systems more than one compound is formed, while others exhibit weak compound formation (*incongruently melting compound*).

Other types of solid–liquid equilibria are found with two components of similar chemical type; if they are isomorphous they may form a *continuous series of solid solutions* (with or without a maximum or minimum in the f.p. curve).   If the miscibility of the components in the solid state is only partial (the pure components not being isomorphous), then a general eutectic or a peritectic f.p. diagram is obtained.

Solid–liquid equilibria are generally investigated by *thermal analysis*—that is, a study of the temperature-time curves obtained when the liquid is slowly cooled. Suppose, for example, the components X and Y form a simple eutectic system, and imagine a certain mixture prepared and melted and then placed in a shielded container and allowed to cool. At first its temperature would fall regularly along a curve *AB* (Fig. 7.8) until the f.p. point of the solution were reached,

Fig. 7.8. Typical cooling curve for a binary liquid mixture forming a eutectic.

at which the liquid became saturated with X. With crystallization of X there would be a reduced rate of fall of temperature owing to evolution of latent heat, but, since the solution would be constantly growing more concentrated in Y, the f.p. would not remain constant but would fall along a curve such as *CD*. In practice, the transition from *AB* to *CD* is rarely ideal; more often a solution *supercools* below its true f.p., *B*, to some temperature *B'* and then, when crystallization of X does commence, there is a sudden evolution of heat which temporarily sends the temperature up to *C'*.

Eventually the solution reaches saturation with respect to Y as well as X.   When this occurs, solid X and solid Y continue to crystallize out side by side in the same proportions as they are present in the solution; the temperature therefore remains constant—the eutectic point.   Finally, when the last drop of solution has solidified and the system consists entirely of solid X and solid Y, the solid mixture continues to cool along the line *EF*.

EXPERIMENT

Determine the f.p. curve of mixtures of ortho-nitrophenol and para-toluidine.

The f.p. of mixtures of *o*-nitrophenol and *p*-toluidine can be determined in essentially the same manner as the f.p. of aqueous solutions (p. 107). A test-tube closed by a cork through which pass a thermometer (graduated in tenths) and a glass rod, the end of which is bent into a loop to serve as a stirrer, is used as the f.p. tube. It is supported by means of a cork ring in a wider tube which acts as an air-mantle.

After weighing the f.p. tube, a quantity of one of the components is placed at the bottom of the tube, and its weight ascertained. Sufficient of the substance must be taken to ensure that, when molten, it completely covers the bulb of the thermometer. The cork with thermometer is now inserted and the tube, surrounded by its air-mantle, supported in a beaker of water. The temperature of the bath is raised until the substance melts in the f.p. tube. The bath temperature is then allowed to fall very slowly, and the temperature of the molten substance read off at intervals of half-a-minute or a minute. Stir the molten mass slowly all the time. At a certain point it will be found that crystals begin to separate from the molten mass and the temperature rapidly rises and remains constant. This constant temperature is the f.p. of the one component. Repeat the determination once or twice.

Now add, from a weighed tube, a quantity of the second component, raise the temperature until all the solid has melted and then allow it to fall slowly and as uniformly as possible. Plot the cooling curve (temperature against time) and note the temperature at which there is a "break" in the cooling curve. Allow the temperature to fall still further until another arrest is shown on the cooling curve and the temperature remains constant until complete solidification takes place. This is the eutectic point. For each composition of the mixture, note the eutectic temperature reached and also the time during which the temperature remains constant at the eutectic point.

Make further additions of the second component, and determine the cooling curve, f.p., and eutectic temperature for each mixture. Mixtures varying in composition by about 10% of the added component should be made.

Results. Plot the values of the f.p. (as ordinates) against composition in mole fractions as abscissae.

With *o*-nitrophenol + *p*-toluidine a diagram showing two curves meeting at the eutectic point is obtained. Other organic systems suitable for study in the manner described above are naphthalene–*p*-nitrotoluene; naphthalene–α-naphthylamine; phenol–urea.

Phase diagrams are particularly important in the chemistry of processes at higher temperatures, e.g. in connection with alloys, bricks, refractories, etc., and consequently thermal analysis is most often carried out with thermocouples.[1]   Quite small thermal changes can be detected by *differential thermal analysis*.[2]   In this technique the two junctions of a thermocouple are embedded in similar masses of material which are heated together in a furnace, but one material is inert to heating while the other undergoes a thermal process, e.g. evolution of moisture, recrystallization, etc.   The thermocouple then shows a temperature difference between the materials when such a process occurs.

The following experiment illustrates the use of a thermocouple for simple thermal analysis at moderate temperatures (300–500° C).
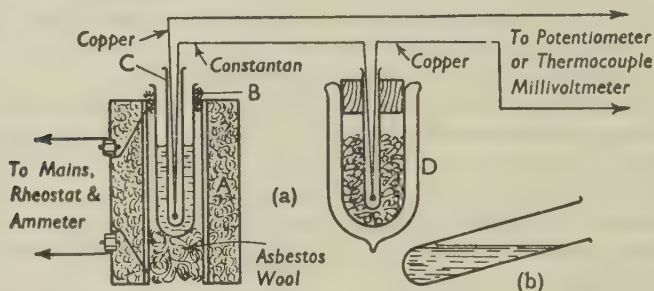
Fig. 7.9. Determination of cooling curves by means of a thermocouple.

EXPERIMENT

Determine the phase diagram of the system $PbCl_2$–KCl.

The apparatus is shown diagrammatically in Fig. 7.9 (a).   *A* is a small electric furnace constructed with Nichrome wire, and controlled by a rheostat and ammeter in series with the mains (see p. 55–6).   The melts are prepared in hard-glass test-tubes ("Pyrex" or "Monax"), and temperatures are measured by a copper-constantan, or, better, chromel-alumel thermocouple encased in a "Pyrex" sheath *C*.   The cold junction is kept in melting ice in a small Dewar vessel *D*.   The temperature is best measured on a potentiometer (p. 248), but a thermocouple millivoltmeter can be used (p. 42).

Procedure.   First the thermocouple must be calibrated by means of pure zinc, lead, $PbCl_2$ and KCl (m.p. 419·5°, 327·4°, 501°, 770·3°C, respectively).   Samples of each are melted in turn in the furnace and stirred with the thermocouple sheath.   The current is cut off and the melt allowed to cool, with stirring, until a steady thermocouple reading is obtained.   A graph of temperature against reading is then

plotted, a smooth curve drawn, and this is subsequently used for obtaining the f.p. of the binary mixtures.

A number of $PbCl_2$–KCl mixtures are made up by weight in separate test-tubes. Each mixture in turn is melted and a cooling curve is determined, temperature readings being taken every 15 seconds. Immediately the sample has solidified the furnace is switched on again and the sample re-melted. The thermocouple is then withdrawn and the test-tube is taken out of the furnace, tilted as shown in Fig. 7.9 (b) and allowed to cool. If this procedure is followed, the tube and mixture can be saved for future use, whereas if the melt is allowed to set with the tube vertical it is liable to crack the test-tube.

Finally, a phase diagram is constructed and interpreted.

Alloy systems. The Pb–Sn eutectic and the Sn–Mg (compound) systems are suitable for study; the latter, however, requires temperatures up to 800° C.

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7E. EQUILIBRIA BETWEEN LIQUIDS AND VAPOURS

Boiling-point curves of two miscible liquids. If the external pressure is maintained constant, the b.p. of a mixture of two completely miscible liquids will vary with the composition. When the curve of total v.p. shows neither a maximum nor a minimum, the b.p. curve will also show neither a maximum nor a minimum, and the b.p. of all mixtures will be intermediate between the b.p. of the pure components. The line, however, will show a curvature which will be all the greater the more widely the b.p. of the components are separated. When a solution which gives such a b.p. curve is distilled, the vapour (distillate) will be richer than the liquid in the component of higher v.p., and the b.p. will rise as the distillation proceeds. By repeated fractional distillation of such a solution, or by distillation through an efficient fractionating column, a complete separation of the two components may be effected.

When the v.p. curve of the liquid solutions passes through a maximum the b.p. curve will pass through a minimum, and when the v.p. curve passes through a minimum the b.p. curve will pass through a maximum. In such cases, a separation of the mixture into its pure components cannot be effected by distillation, but only a separation into one or other of the components and a mixture of constant b.p. (*azeotropic mixture*), the composition of which corresponds to the maximum or minimum point on the b.p. curve.

EXPERIMENT

Determine the equilibrium liquid-vapour curves for binary mixtures of completely miscible liquids.

The b.p. curves should be determined for one or more of the following binary systems, which are representative of the three classes referred to above:

(i) *Zeotropic mixtures*, with b.p. intermediate between those of the pure components: (a) benzene (80·2°)–toluene (110·6°): (b) benzene–hexane (69·0°).

(ii) *Azeotropic mixtures with minimum b.p.:* (a) *iso*-propyl alcohol (82·5°)–benzene (azeotropic mixture 71·9°, 39·3 mole % of alcohol). (b) carbon tetrachloride (76·8°)–methyl alcohol (64·7°) (azeotropic mixture 55·7°, 44·5 mole % of CCl$_4$): (c) methyl alcohol–benzene (azeotropic mixture 58·3°, 61·4 mole % of alcohol).

(iii) *Azeotropic mixtures with maximum b.p.:* (a) chloroform (61·2°)–acetone (56·4°), (azeotropic mixture 64·5°, 65·5 mole % of CHCl$_3$): (b) water (100°)–formic acid (99·9°), (azeotropic mixture 107·1°, 43·4 mole % of water).

Procedure. Prepare binary mixtures containing 10, 20, 40, 60, 80, 90 mole % of one of the components, and determine the refractive indices of each mixture at a definite temperature (15–20°), using a Pulfrich or Abbe refractometer, and also the refractive index of the pure components. Draw, on a moderately large scale, a graph showing the relation between composition and refractive index.

First determine the b.p. of the pure components so that the thermometer readings may be checked and any necessary correction introduced. Then determine the b.p. of each of the mixtures and the equilibrium composition of the vapour and of the liquid. For this purpose a quantity of the mixture (70–80 ml) is placed in a boiling-tube as shown in
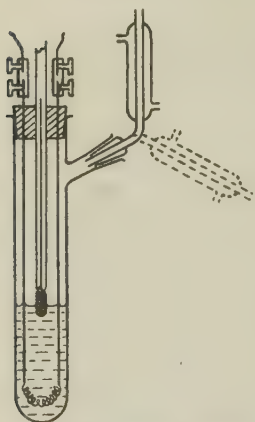
FIG. 7.10. Simple apparatus for determination of vapour – liquid equilibrium diagrams.

Fig. 7.10. The boiling-tube is fitted with a standard ground glass joint and carries a small condenser. The tube is placed in a Dewar vacuum vessel. The apparatus is fitted up so that the liquid can be heated electrically, as shown in the Figure. A thermometer, graduated in tenths of a degree, passes through the cork fitted in

the mouth of the boiling-tube, so that the bulb is partially immersed in the liquid. (For the best accuracy one must use the Cottrell apparatus to avoid errors due to superheating (see p. 118).) The liquid is now caused to boil steadily until vapour is freely forming liquid in the condenser. When the temperature of the liquid has become constant, it is noted and the condenser is then rotated so that the condensate runs out into a small, cooled weighing bottle. After about 0·5–1 ml of liquid has been collected (do not collect too much), the heating current is cut off, the cork is removed from the boiling-tube and a small quantity of liquid is removed and run into a small weighing bottle, which is then stoppered and cooled. The refractive indices of the distillate and of the liquid in the boiling-tube are determined under the same conditions as before, and the composition of the boiling liquid and of the vapour in equilibrium with it (the distillate) is read from the composition-refractive index curve.

Proceed in the manner described with each binary mixture, and plot the molar percentage composition of liquid and vapour at each boiling temperature in a temperature-composition diagram.

Separation of mixtures by distillation. The vapour in equilibrium with a solution of two volatile liquids is richer than the liquid in the component of higher v.p. (lower b.p.), and, consequently, when the liquid mixture is fractionally distilled, each fraction will be richer in the more volatile component than the liquid from which it is distilled. By subjecting these "fractions" to further fractionation, distillates can be obtained which are progressively richer and richer in the more volatile component, until, in the case of zeotropic mixtures, a complete separation of the components is effected.

When distillation is carried out with a fractionating column, repeated distillation of the fractions is avoided. When distillation is in progress, a temperature gradient is established along the column and, on passing upwards, the vapour which condenses is increasingly rich in the more volatile component. In other words, a process of repeated distillation takes place in the column, and, under theoretically perfect conditions, the pure component of lower b.p. collects in the condenser, and the component of higher b.p. is left in the still.

In the case of liquids which form binary azeotropic mixtures, separation into the two pure components cannot be effected by distillation, but only into an azeotropic mixture and one or other of the components, depending on the initial composition of the mixture. In the case of liquids which give a b.p. curve showing a minimum, the azeotropic mixture will be obtained as the distillate, and the residue will be one or other of the components. When the b.p.

curve shows a maximum, the distillate will be one or other of the components, and the azeotropic mixture will be left in the still.

After having obtained the b.p. curves for a series of binary mixtures, the separation of these mixtures by distillation should be studied, and the efficiency of different fractionating columns investigated. The constant boiling mixtures, also, should be prepared by distillation, and their composition be thereby more accurately determined.

Owing to the great importance of distillation, the theory and technique of the process have received great attention. Rather elaborate apparatus is nowadays used in determinations of vapour–liquid equilibria.[1] The efficiency of fractionating columns is tested by means of standard zeotropic mixtures, e.g. CCl_4–C_6H_6, and is expressed as the "H.E.T.P. number", that is, "*height equivalent to a theoretical plate*". This means the length of the column required to produce in practice as much separation as one ideal vapour–liquid *equilibrium* would effect. The practical separation obtained depends on the *reflux ratio*, i.e. the proportion of vapour which is condensed and permitted to return down the column; the greater the reflux, the better the separation. For the details of the theory and technique of fractional distillation, one of the monographs cited below should be consulted.

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OPTICAL MEASUREMENTS IN CHEMISTRY

8A. LIGHT SOURCES

1. Continuous spectrum sources. The tungsten filament lamp is a convenient source of light for microscopy and absorptiometry in the visible region of the spectrum. It gives a *continuous* spectrum, having maximum intensity in the near infra-red, and falling off to zero in the near ultra-violet. A short-filament or headlamp bulb used at a voltage slightly in excess of the normal rating gives a higher relative intensity at the violet end of the spectrum extending also into the ultra-violet. This source is particularly suitable for *photo-microscopy* when ordinary (not panchromatic) plates are used. In the *Pointolite lamp* a sphere of tungsten heated to incandescence forms a small source of high intrinsic intensity; for still higher intensities the *carbon arc* is used but is less convenient and does not give a reproducible intensity.

The *hydrogen discharge lamp* is the source employed for absorption spectrometry in the ultra-violet; an electric discharge through hydrogen at a few mm pressure gives a light of a pale mauve colour which is found to consist of a number of discrete lines* in the visible spectrum (Balmer series), leading to a continuum in the blue and ultra-violet. Two forms of hydrogen lamp are in use. The large, water-cooled, high-voltage tubes consist of two electrode compartments separated by a length of narrow tubing through which the discharge passes. This tube is observed from the end through a window of quartz. Large hydrogen tubes of this type require 2,000–5,000 V and consume 1–3 kVA. They are being superseded by the low-voltage type. These consist of a small, oxide-coated tungsten filament surrounded by a cylinder of tungsten. The discharge passes through a rectangular slit in the screen under a potential of about 100 V, giving an intense, localized light source.

An arc or condensed high-voltage spark between tungsten-steel rods is sometimes used as a quasi-continuous source for visible and ultra-violet absorption spectrometry. Its spectrum contains a very large number of sharp lines.

2. Line spectrum sources. Small *gas discharge tubes* containing a low pressure of hydrogen, helium, argon, neon, etc., provide sharp

*A short table of prominent lines is given in the Appendix, Table A8.

149

line spectra suitable for calibrating spectrographs in the visible region of the spectrum. The old Geissler tubes were H-shaped, the discharge being observed along the axis of the horizontal section; they required a small current at high voltage from an induction coil or high-voltage transformer. More compact helium, argon and neon lamps working from the 220 V d.c. mains can be obtained.[1]

Metallic vapour lamps provide the most convenient sources of line spectra of high intensity. The "Osram" laboratory lamps, containing sodium, cadmium, mercury, or mercury+cadmium, made by the General Electric Co., Ltd. (London), are particularly valuable for spectrograph calibration, refractometry, polarimetry, etc. The
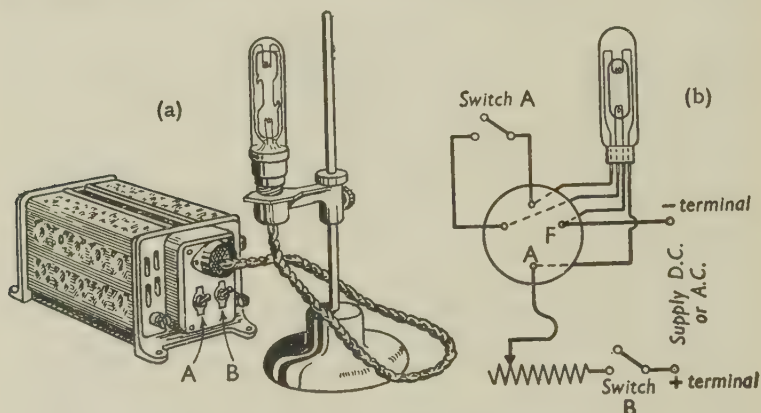
FIG. 8.1. Laboratory metal vapour discharge lamp.
(a) "Osram" lamp and rheostat. (Courtesy General Electric Co. Ltd., London).
(b) Wiring diagram.

spectra of these metals give a number of intense, well-separated lines of known wavelength, which can be isolated by use of filters or a spectrometer to give monochromatic light of various wavelengths. The "Osram" lamps (Fig. 8.1) contain a low pressure of inert gas and a quantity of the volatile metal. The electrodes consist of two tungsten filaments which are initially heated for about 1 minute by passage of a current. This induces thermionic emission from the filaments so that when the heating current is switched off and the full mains voltage applied across the tube, a discharge strikes between the electrodes, being carried initially by the inert gas. As the heat of the discharge vaporizes the metal, the metallic spectrum grows in intensity and supersedes that of the inert gas.

The *sodium lamp* is the usual source for refractometry and polarimetry, as it provides almost monochromatic light—about 99% of

the visible radiation emitted by it lies in the 5,890–5,896 Å doublet ("D lines"). If necessary, the faint red, green, and blue lines can be almost completely absorbed by passing the light through a few cm of 7% aqueous potassium dichromate solution or equivalent glass or gelatine filter. The 45-watt sodium lamps used for street lighting are also very suitable for polarimetry.

Mercury vapour lamps are particularly useful when light of several wavelengths in the visible or ultra-violet is needed as in determinations of optical dispersion, in photochemistry, and ultra-violet photomicroscopy. Many types of lamp are available. The "Osram" mercury lamp is convenient for refractometry in the visible region. Small street-lighting mercury lamps give larger sources of visible and near ultra-violet light. The small quartz mercury discharge tubes employed in commercial "black" lamps (for exciting fluorescence) are very intense in the visible and ultra-violet. A small source of still greater localized intensity, particularly suitable for producing a focused beam, is provided by lamps in which a heavy discharge is passed between stout tungsten rods enclosed in mercury vapour in a silica bulb.

Several types of mercury discharge lamps are suitable for irradiating solutions, paints, etc. The chief distinction between them is the pressure at which they operate; low pressure lamps, operating at about 5,000 V, emit a high intensity of the mercury resonance line at 2,537 Å. Higher pressure lamps (running hot) show reversal of this line owing to self-absorption, and give greatest intensity in the 3,650 Å line. Dark goggles should always be worn when working with ultra-violet lamps. The harmful rays are largely cut off by ordinary glass.

3. Filters. When a more or less monochromatic source of light is needed, as in "colorimetry" (absorptiometry) and photochemistry, some form of filter may be applicable. Liquid solutions, coloured glasses, and dyed gelatine films are often used. It should be realized that the absorption bands of all filters are relatively broad and gradual in onset. Consequently, the ideal complete cut-off of some regions of the spectrum and complete transmission of a narrow region are rarely obtained. A green filter, for example, would transmit a little yellow and blue light when used with a continuous spectrum source. However, the principal well-separated lines of the mercury spectrum can be isolated in fairly pure form by use of combinations of liquid, glass, or gelatine filters. Glass filters are also available for absorbing infra-red (heat rays) and for transmitting the near ultra-violet while absorbing the visible ("black glass").

The so-called "interference" filters, first used by Christiansen,[2]

are now becoming commercially available (e.g. from Messrs. Barr & Stroud, London); they consist of a suspension of glass powder in a liquid of similar refractive index, and have the advantage of a rather narrow transmission band.

When light of very high purity is needed, a single or double *monochromator* is used. This instrument is essentially a spectrometer of large aperture.

BIBLIOGRAPHY 8A: Light sources

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[1] E.g. from Messrs. Hilger and Watts, Ltd., London.
[2] Christiansen, *Koll. Zeit.*, 1939, **86**, 55.

8B. EMISSION SPECTRA*

When a substance in the gaseous state is *excited* by high temperatures or electric discharge, it may emit light, and, owing to the quantization of the permitted energy levels of atoms and molecules, the light will consist of quanta of definite size (or sizes) and hence will give a *line spectrum*. It is well known that the wavelengths, λ, (or frequency ν, or wave-number, $\tilde{\nu}$, where $\tilde{\nu} = 1/\lambda$, and $\nu \times \lambda = c$, the velocity of light) of lines of emission spectra are highly characteristic of each substance. Spectrum analysis has therefore long been used for detecting the presence of various elements, and is nowadays extensively employed in routine quantitative analysis (e.g. of alloy steels). Quartz ultra-violet spectrographs of high dispersion are generally used for spectrographic analysis, but the principles of spectrum analysis can be readily illustrated by reference to the glass wavelength spectrometer described below. (It is assumed that the reader is already familiar with the ordinary rotating turntable spectroscope—an instrument rarely used nowadays in chemical laboratories).

The constant deviation spectrometer. The determination of wavelengths of spectral lines is rendered very simple by using a spectrometer graduated so that wavelengths can be read directly on a scale. This is the case with the constant deviation spectrometer: the telescope and collimator are fixed at right angles, while the special prism can be rotated by a calibrated micrometer screw. Fig. 8.2 shows the form of this instrument made by Messrs. Hilger and Watts, Ltd. (London), without the prism casing. The collimator tube *A* carries an adjustable slit *B* and simple shutter *C*. The constant deviation

* The brief introduction to spectroscopy contained in sections *B* and *C* is confined to visible and near ultra-violet spectra. Although the same general principles apply to other spectral regions, the techniques employed in infra-red and for ultra-violet spectroscopy are too specialized for consideration here.[1]

prism D has the form shown in Fig. 8.3 (a), from which it can be seen that the ray which travels in the prism exactly parallel with the diagonal BD will emerge exactly at right angles to its original direction whereas rays of other wavelength, being differently refracted,
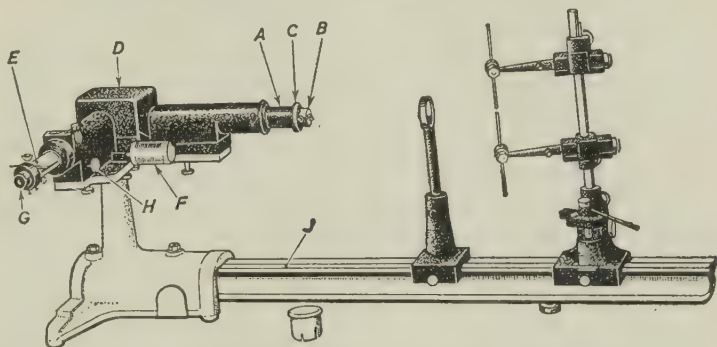
FIG. 8.2. Constant deviation spectrometer: general view.
(Courtesy Messrs. Hilger and Watts, Ltd., London.)

emerge in different directions.   However, for each wavelength there is one position of the prism which would permit the ray to enter the telescope E.   The setting of the prism therefore determines the wavelength of light which will be observed at the centre of the eye‐piece, G.   The rotation of the turntable carrying the prism is effected
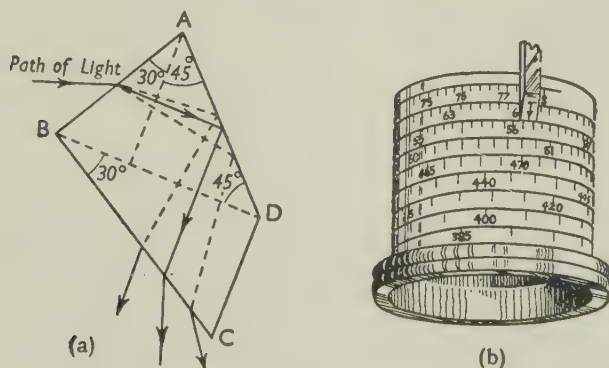
FIG. 8.3. Constant deviation spectrometer.
(a) Path of rays through the prism.   (b) Wavelength drum.

by a micrometer screw, the hardened point of which presses against a polished steel plug in the projecting arm attached to the table. The screw carries a drum, F, (see Fig. 8.3 (b)) on which a pre-determined wavelength scale has been engraved.   This scale is dependent

on the dispersion of the prism, but with a given instrument the wavelength can be read off directly as indicated by the index.   Focusing of the telescope is effected by means of a milled knob, *H*.   The telescope eyepiece, *G*, contains a pointer which can be adjusted laterally; it is brought into focus by turning the eyepiece.   The bar, *J*, is for mounting accessories such as light source, lenses, etc.

Once the spectrometer has been set up the prism should not be touched, but the following adjustments and checks can be made: (1) slit width, (2) verticality of slit, so that the image of a line is parallel with the slit in the eyepiece, (3) focus of eyepiece on the pointer, (4) focus of telescope for sharpness of spectra – separation of the Na-D lines is a good test.   The accuracy of setting of the instrument can then be checked by reading the wavelengths of a number of well-defined spectral lines such as those of sodium and mercury (Appendix, p. 355).   Once the scale has been checked (or calibrated) the instrument can be used to determine the wavelength of spectra.
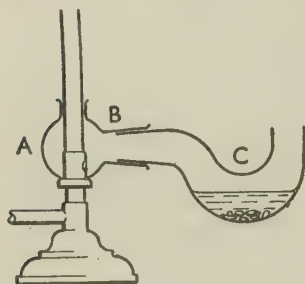
FIG. 8.4. Device for producing persistent flame spectra.

EXPERIMENTS

A. Examine the light emitted when the chlorides of sodium, potassium, lithium and thallium are vaporized in a Bunsen flame.

B. Measure the wavelengths of as many as possible of the lines of the hydrogen spectrum, and compare the values obtained with those calculated from the expression: $\lambda = 3,645 \cdot 6 \left(\dfrac{m^2}{m^2 - 4} \right)$, *where m is successively given the values 3, 4, 5, etc.*   (*Balmer Series.*)

Procedure: A. The substances may be volatilized from a clean platinum wire or fibrous asbestos wick, but a more persistent flame is obtained with the device shown in Fig. 8.4.   A glass bulb *A* with side tube *B*, is placed over the tube of the Bunsen burner, so that the side tube is opposite the air inlet of the burner.   Fitting into *B* by means of a ground joint is another tube *C*, of the shape shown.   Into the well formed by the bend in the tube *C*, is placed a concentrated solution of the salt under investigation, together with a few pieces of zinc.   A few drops of copper sulphate solution are added in order to coat the zinc with copper.   On adding a little dilute hydrochloric acid, hydrogen is generated which, escaping from the solution in fine bubbles, gives rise to a spray.   When the gas is burning at the Bunsen this spray is carried by the current of air into the burning

gas and produces the coloured flame. The lines observed in the flame spectra should be classified roughly according to intensity, e.g. very strong, strong, medium, weak, very weak.

Results. The lists of wavelength recorded should be compared with standard tables of spectral lines. The presence of impurities should be looked for, e.g. Na in K salts and vice versa, Rb in K, etc.

Spectrography. The scope of spectrum analysis is greatly extended if the spectra are recorded photographically. In the ultra-violet this method is, of course, indispensable unless a sensitive photo-electric spectrophotometer is available.

The eyepiece of the telescope of the Hilger wavelength spectro-meter (Fig. 8.2) can be removed and replaced by a quarter-plate size camera bearing a rack and pinion by which the plate may be moved vertically, so that a number of spectra can be photographed on the same plate. Before exposures are made, it is necessary to make the following adjustments: (1) slit width, (2) slit height (for width of spectrum), (3) focus of telescope for sharpness of image on the plate, (4) angle of tilt of the plate holder. These adjustments can be made with a ground-glass screen in the plate holder, the image of a suitable line source being examined usually with the aid of a hand lens, but the final setting is best found from a number of trial photographs.

The proper alignment of the source on the optical axis of the colli-mator requires careful attention. A good method of locating the correct position for a small source such as an arc or spark is to place a lighted flashlight bulb in the position that will be occupied by the centre of the spectrum, and to trace back the image of this source where it emerges from the collimator; a darkened room is, of course, necessary for this operation.

Since a small source such as an arc or spark will not illuminate the whole of the slit uniformly (if placed close) or sufficiently intensely (if placed far from it), an auxiliary lens is usually employed to cast an enlarged image of the source on to the slit (Fig. 8.2). The source should be situated at 4–5 times the focal length of the lens from the slit.

When a spectrum is to be photographed, it is necessary to record on the same plate a spectrum of a known source to provide a wave-length scale. The Hilger wavelength spectrometer bears a small movable prism on the collimator so that light, for example, from a mercury lamp placed at the side, can be reflected into the slit to provide this reference spectrum. The spectrum should be recorded on the top and the bottom of the plate.

The type of photographic plate to be used will depend on the part of the spectrum concerned. "Ordinary" (Process) plates are

sensitive only to the blue, violet and ultra-violet: "orthochromatic" are also sensitive to green and yellow, but can be processed safely in dim ruby-red light: "panchromatic" are sensitive to all parts of the visible spectrum, and must therefore be loaded and developed in total darkness. Special "infra-red" plates extend the photographic range to about 12,000 Å. A plate giving good "contrast" is desirable for spectrography, e.g. Ilford "Xenith" (ortho, to 5,700Å) and Ilford "Rapid Process Panchromatic" plates. Any normal developing and fixing solutions can be used.

EXPERIMENT

Photograph a copper arc spectrum and use it to construct a wavelength calibration chart for the spectrograph.

Procedure. Two rods of high purity copper should be mounted in an insulated, adjustable stand (Fig. 8.2). The arc gap must be aligned with the optical axis of the collimator (see above). The arc is best run from d.c. mains with an adjustable rheostat of adequate current carrying capacity and ammeter in series. A current of 5 amp is suitable. The arc is easily struck by drawing a carbon rod (on an insulated handle) across the gap between the electrodes after the current has been switched on. The optimum size of gap and value for the series resistance to produce a steady arc is found by trial.

Next, the auxiliary condenser can be set, and a convenient slit width and height can be selected. The wavelength drum should, of course, be set to a suitable position and subsequently not altered. A trial plate can then be exposed, using a range of different exposure times, in order to find a suitable exposure. The best focus and tilt of the spectrograph can next be determined by taking another plate with a number of different settings (all near the visual optimum). This plate should be dried and then examined carefully with a lens to ascertain the settings which give the sharpest lines over the spectral range to be investigated.

Finally, when all the adjustments have been made so that sharp, uniform spectra are attained, the calibrating plate can be taken. The spectrum of a mercury lamp should also be recorded on top and bottom of the same plate. A full record of all the details of the exposures should be made. After processing, the plate can be labelled by writing on the edge with ink.

Construction of calibration chart. When the plate is dry, the positions of as many as possible of the lines of the mercury and copper arcs are to be measured. It is convenient to adopt one particularly prominent and easily identified Hg-line as origin. A straight edge of metal is laid across the plate (the gelatine being uppermost) and carefully aligned with the chosen Hg-line on the

two sides of the plate: a fine line is then drawn in the gelatine with a razor blade right across the plate and passing precisely through the centre of the chosen line in the two Hg-spectra.

The distances, positive or negative, of other lines of the Hg- or Cu-spectra can now be measured, taking the mark as origin. The measurements should preferably be made with a travelling microscope.

Next, it is necessary to identify the measured lines by reference to tables of wavelengths. The lines of the mercury arc are fairly easily recognized by inspection of published spectrograms. The general form of the dispersion curve, i.e. wavelength against distance along the plate, can then be drawn, and points for the Cu-spectrum can then be added by reading approximate wavelengths from the provisional chart and then identifying the lines in lists of characteristic wavelengths.

Finally, an accurate graph on a large scale can be drawn, plotting wave-number or frequency of the lines against distance from the reference line. This chart will then serve to characterize lines of other spectra which may subsequently be photographed with the same specified setting of the spectrograph.

Spectrographic analysis. The *qualitative identification* of elements requires that the substance be volatilized. The flame excitation method previously described (p. 154) is effective for only a few elements, and it is therefore more usual to employ the high temperatures of the carbon arc or of a high-tension spark to volatilize and excite the spectrum of a mixture which is to be examined. Solids can be excited by embedding them in a cavity in the centre of the electrodes of a carbon arc. Solutions can be excited by use of the Zehden sparking tube.[2]

For *quantitative* spectrographic analysis means must also be provided for measuring the *relative intensities* of selected spectral lines. Standard mixtures of known analysis must be used for comparison since there is no simple way of arriving at the percentage of an element in a mixture from a measured intensity. Further, the absolute intensity of an arc or spark is not reproducible from one sample to another. Consequently, a comparison is made between the intensities of two lines, one from, say, the substrate and the other from the substance (e.g. impurity) to be determined. For example, to determine Cu in steel, one may compare the intensities of a characteristic Cu-line and an Fe-line, a similar comparison being made also for a series of steels of different, known Cu content. Methods of measuring relative line intensities include photographic and photoelectric photometry.[3] (See p. 161 for principles of these methods of photometry.)

In the preparation of standard mixtures for spectrographic analysis one needs chemicals of exceptional purity. Such chemicals are available under the title of "spectrographically pure", but they are, of course, very expensive.

EXPERIMENT

Make a spectrographic examination of a sample of strontium carbonate for the presence of barium.

Procedure. Use the spectrograph which has been calibrated as described in the preceding experiment. Set up a carbon arc with high-purity ("spectroscopic") carbon electrodes, making the lower electrode positive. The arc requires about 60 V and 5 amp to maintain it; it can therefore be run from the 110 d.c. mains with a 10 ohm, 10 amp resistance. Focus an image of the arc on to the slit of the spectrograph, and select only the centre of the image by means of the wedge or Hartmann diaphragm.

To excite the spectrum of a powder, a small quantity of it is packed into a cavity drilled in the lower carbon electrode.

Photograph (a) the carbon arc alone, (b) the arc with strontium carbonate, (c) the arc with strontium carbonate to which a small amount of barium carbonate (e.g. 0·1%) has been deliberately added.

Identify the principal Sr and Ba lines as far as possible. The persistent Ba lines at 5,777·7 Å and 5,535·5 Å are suitable for detecting traces of barium. A rough estimate of the amount of Ba present can be made by comparing the intensity of the Ba line in the sample with that obtained with spectroscopically pure $SrCO_3$ to which known amounts of $BaCO_3$ have been added (with thorough mixing).

Note that the carbon arc gives bands in the near ultra-violet; these are due to CN (formed as a transient entity in the arc). Other band spectra such as those of CaO, CaF, etc., may be encountered in spectrographic analysis.

Raman spectra. When a beam of monochromatic light is passed through a medium which does not absorb it, a very small proportion of the light is *scattered* in all directions. Only with a colloidal solution is the scattered light perceptible to the eye (*Faraday-Tyndall beam*), but even with a pure, dust-free liquid it is possible to detect scattered light by a suitably long photographic exposure taken, of course, at right angles to the incident beam. (Scattered light must not be confused with fluorescence, which is due to absorption and re-emission; fluorescent light is generally at a longer wavelength than that absorbed).

The light molecularly scattered by a non-absorbing medium is mostly of the same wavelength as that of the incident light, and a

study of the intensity of this scattering forms the basis of an important modern method of determining the molecular size and shape of colloidal particles and macro-molecules.[4]

In addition, however, part of the scattered light is found to have undergone definite displacements of wavelength. The spectrum of the scattered light therefore consists of a strong impression of the spectral line from the source together with a number of other sharp but much weaker lines, some at longer and some at shorter wavelengths than the exciting line. These additional lines are called the *Raman spectrum.*

The differences between the frequencies of the Raman lines and the exciting line can be shown to correspond to certain of the *frequencies of vibration* within the molecule. Raman spectra, observed with visible or ultra-violet light, can therefore give structural information rather similar to that supplied by infra-red spectra.[5]

Experimentally, Raman spectra can be recorded by the glass wavelength spectrograph. It is necessary to use very intense monochromatic illumination of a wavelength well outside any absorption bands of the substance. For example, a mercury lamp of the type used for street lighting can be used in conjunction with a filter consisting of a 1/10th saturated solution of iodine in carbon tetrachloride to provide a nearly pure source of 4,047 Å wavelength. The liquid to be irradiated is contained in a cylindrical glass tube placed alongside the mercury lamp, and the scattered light is photographed through the end of a tube. Precautions must be taken to remove dust and to prevent stray (reflected) light from getting to the spectrograph. Photographic exposures of many hours duration are needed to bring out the faint Raman lines.

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[2] Twyman and Hitchen, *Proc. Roy. Soc.*, 1931, A133, 72.
[3] See, for example, Brode, *op. cit.*
[4] A good review of the method is given by Doty and Edsall, *Adv. in Protein Chem.*, 1951, **6**, 37.
[5] Hibben, *The Raman Effect and its Chemical Applications*, 1939 (Reinhold Publ. Corpn., New York).

8C. ABSORPTION SPECTRA

When a beam of monochromatic light of intensity I_0 passes into a medium which absorbs that wavelength, the intensity is gradually reduced as the beam progresses through the medium, according to Lambert's Law, namely, $\log \dfrac{I_0}{I} \propto d$, where $\log \dfrac{I_0}{I} (= E)$ is called the extinction or optical density, and I is the intensity of the beam after passing through a thickness d of the medium. If the medium is a solution containing one absorbing substance, then (in the absence of chemical reactions) Beer's Law generally applies also; this states that the extinction is proportional to the concentration, c, of the absorbing species. The combined laws therefore give for absorption by a solution:

$$E = \log_{10} \frac{I_0}{I} = kcd$$

The constant k is known as the *molecular extinction coefficient* of the substance since it expresses the extinction resulting from 1 cm of unit concentration of the substance. A graph showing how k varies with wavelength of the light is called the *absorption curve* (or spectrum) of the substance.

Some gases (e.g. I_2 vapour, NO_2) show sharp absorption spectra consisting of series of *bands* containing *fine structure*. These bands correspond to electronic excitation and the fine structure arises from vibrational and rotational excitation. Generally the bands lead to a *series limit* (corresponding to optical dissociation of the molecule) and thereafter a region of *continuous absorption* exists.

The band spectra are much less sharp when the substance is examined in solution instead of in the gaseous state, and in most cases the overlap between adjacent lines and bands is so extensive that a broad region of continuous absorption results; the individual lines can no longer be distinguished and only maxima and minima appear on the absorption curve. The "absorption spectrum" of the substance is then characterized by the wavelengths and intensities of the maxima and minima. The absorption curve depends considerably on the solvent. Much empirical information is available regarding the relation between the absorption spectrum (in the visible and ultra-violet) and chemical structure, particularly of organic compounds.[1]

Absorption spectra have many important applications in analysis, in structure determination and photochemistry, as well as miscellaneous uses such as assessment of colour value of dyes and filters.[2]

Absorption spectrophotometry. An absorption curve is determined by means of a spectrometer used in conjunction with a photometer: the latter measures the ratio I_0/I for each wavelength. A source of continuous spectrum (e.g. tungsten lamp for the visible or hydrogen lamp for the ultra-violet) is employed. Most photometers employ two optical cells, one containing the pure solvent and the other the solution, the light transmitted by the two being compared in some way. In *visual photometers* the amount of light passing through the solvent is gradually reduced to a known degree by an optical device (e.g. diaphragm, adjustable slit, or polarizing prism) until the two beams are judged to match in intensity.

The Hilger-Nutting photometer is an instrument of this type, employing polarizing prisms. It may be combined with the Hilger wavelength spectrometer for visual spectrophotometry. The scale is graduated directly in extinctions, i.e. log I_0/I. A "Pointolite" lamp is the best source.

The Hilger "Spekker" photometer can also be used for visual spectrophotometry in conjunction with the wavelength spectrometer, although its primary purpose is for *photographic photometry* in the ultra-violet. Two spectra, one transmitted by the solvent, the other by the solution, can be observed or photographed side by side. A series of exposures is taken with gradually reduced intensity on the part of the solvent beam. If absorption bands are present one finds by examination of the photographic plate the positions on each pair of spectra at which a *match point* is seen, i.e. where the two beams are of equal intensity. These match points are marked by a spot of ink (on the reverse side), and the corresponding wavelengths are measured off. A graph of extinction against wavelength can thus be constructed. A rather similar method of photographic photometry employs a *rotating sector* to cut down the light intensity by a known factor.

Yet another method of photometry is to photograph the spectra, also making a number of calibrating exposures of known intensity on the same plate, and subsequently to measure the density of the photographic negatives by means of an instrument known as a *microphotometer*.

The most satisfactory method of photometry, however, is by direct measurement of the transmitted light intensity by means of photocells (pp. 163–8). The modern *photoelectric spectrophotometer* consists essentially of a monochromator combined with a photocell. Each wavelength is selected in turn by simply setting a dial, and the beam of monochromatic light passes through either a cell of the pure solvent or a similar cell containing the solution. The transmitted light falls on to a photocell, the current of which is amplified and

indicated on a robust pointer instrument. Only a few seconds are needed to determine the ratio of I_0/I at each wavelength, and consequently photoelectric spectrophotometers are rapidly displacing the more laborious instruments previously used.

EXPERIMENT

Determine the absorption curve of a coloured substance in solution, and examine the validity of the laws of Lambert and Beer. (*Suitable solutions*: I_2 in CCl_4, K_2CrO_4, $CuSO_4$, $KMnO_4$ in water.)

Procedure. Any available spectrophotometer may be used. Prepare a range of solutions differing in concentration by factors of 2. By trial find the most suitable concentration for determining the shape of the absorption curve using a 1 cm cell; the maximum absorption should be about 90%. Determine the absorption at a sufficient number of wavelengths to permit the absorption curve to be drawn accurately. Lambert's Law can now be tested by measurements with 10 cm, 1 cm, and 1 mm cells. (A Baly tube of adjustable length may be used.) Beer's Law can be tested by measurements with solutions of different concentration. These two latter parts of the experiment may be confined to one wavelength—say in the region of the maximum of absorption.

Results. Draw the absorption curve of the substance (extinction coefficient against wavelength) and report the wavelength and extinction coefficient at maxima in the curve.

If Lambert's Law holds, the extinction ($\log I_0/I$) should be proportional to the cell length. If Beer's Law holds, the extinction should be proportional to the concentration.

Other experiments, (1) The absorption curve for mixtures may be investigated. Provided no chemical interaction occurs, the extinction of the mixture is the sum of the extinctions due to the separate absorbing substances.

(2) The absorption curve of a pH indicator in a series of buffer mixtures of known pH may be studied (cf. section 12F).

(3) The spectrophotometer can be used to investigate the formation and stability of coloured complexes (cf. p. 124).

(4) The *diffuse reflection spectra* of pigments can be determined.

(5) *Fluorescence spectra* emitted by solutions or solids (phosphors) under excitation by ultra-violet light can be photographed.

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8D. LIGHT INTENSITY: PHOTOCELLS AND COLORIMETERS

Many useful analytical determinations can be made by measuring the intensity of colour produced by a specific reagent (e.g. determination of ammonia with Nessler's solution).   The various instruments designed for this work have been traditionally called "colorimeters"; since they measure not the colour but its intensity, they are more appropriately termed "absorptiometers". (The Lovibond tinto-meter, however, is capable of measuring colour as well as intensity on an arbitrary scale.)   Early colorimeters depended on visually matching the intensity of the test solution with that of a "known". This was done either by changing the concentration of the "known" or by altering the path length; the Duboscq colorimeter, for instance, is an instrumental development of the simple Nessler cylinders and permits intensities to be matched, under favourable conditions, with an accuracy of 1–2% by changing the effective depth of the solution. The Pulfrich photometer matches the beams transmitted by solvent and solution by reducing the former to a measured extent by means of an adjustable aperture.

Such *subjective* photometers are being superseded by photo-electric instruments; the latter are rarely more accurate than the best visual photometers, but are cheaper and less subject to personal errors, and can be used in the near ultra-violet or infra-red.

Light energy (visible, ultra-violet, or infra-red) can be converted into electrical energy by means of (a) its heating effect, or (b) the photoelectric effects.   The former is employed in radiation thermo-piles, and bolometers; these are used for detecting and measuring the intensity of light used in photochemical experiments.   However, the various types of cell based on the photoelectric effect provide much more sensitive detectors of visible and ultra-violet light and are therefore used in photometers.

Photocells.   The chief types of photocell are those depending on photo-emission and those employing the photo-voltaic effect.*

Photo-emissive cells consist of a metal plate cathode A (Fig. 8.5) and a wire frame anode B contained in a sealed glass bulb which is either evacuated or contains a low pressure of argon.   When light falls on the cathode electrons are emitted, and these can be collected by the anode.   In a vacuum photocell 20–90 V is sufficient to collect all the photo-electrons ("saturation current").   In a gas-filled cell any increase of voltage above about 20 V causes an increase

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* Photo-conduction cells depending on the change of electrical resistance of a thin film of selenium when illuminated are little used in photometry as they suffer from "fatigue".   However, a photo-conductive cell containing a film of lead sulphide has recently been developed for measuring infra-red radiation in the region of 22,000 Å.

of current owing to collision-ionization of the gas. This additional current makes the gas-filled cell more sensitive than the vacuum cell ("gas amplification"), but the maximum safe magnification is about 10 times, and 5 times is usually chosen, corresponding to about 90 V on the anode.

Vacuum photocells (or gas cells at low voltage) are chosen for photometry as their characteristics are more reproducible and the anode current is closely proportional to light intensity.

Sensitivity of emission photocells. The *sensitivity* of photocells to visible light is often expressed in terms of microamperes per lumen, but this is not an entirely satisfactory basis as the spectral distribution of the light is important. The lumen is the unit of luminous *flux*, and is based on the "standard candle". One candle placed at 1 ft from a surface produces an *intensity of illumination of 1 ft-candle*. The total flux falling on 1 sq. ft of surface illuminated with 1 ft-candle is 1 lumen; thus, lumens = intensity of illumination (in ft-candles) × area (in sq. ft). One candle emits 4π lumens. (The lux = 1 metre-candle, and lumens = lux × area in sq. m).
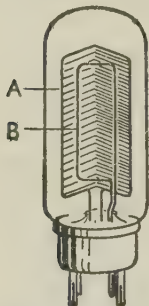
FIG. 8.5. One form of emission photocell.

The luminous efficiency of incandescent lamps can be expressed as the number of lumens emitted per watt of electric energy consumed. It is useful to know that a modern 60-watt gas-filled tungsten filament lamp has an efficiency of about 13 lumens per watt, which is just 1 candle-power per watt.

Typical photocell sensitivities to visible light (from a tungsten lamp) are 15 μA/lumen for vacuum and 75 for gas-filled cells having a caesium-silver oxide cathode, and 120 μA/lumen for gas-filled caesium-antimony cells.

The spectral response of photocells is best expressed in terms of milliamperes of current passed by the cell when a flux of 1 watt of monochromatic radiation falls on the cathode. Fig. 8.6 shows that a cathode composed of a thin film of oxidized caesium on silver has a maximum of sensitivity in the near infra-red and another in the near ultra-violet. The potassium cell (curve *B*) can be used for the blue end of the spectrum, but it is now being displaced by the thin-film caesium-on-antimony cell which has a much higher sensitivity in this region (curve *C*). A sodium cell has a maximum response at about 3,000 Å and is therefore used in a cell with a quartz window for measurements in the ultra-violet.

Circuit for photocells. Light of moderate intensity (say, about 0·01 ft-candle upwards) can be measured without amplification by means of a sensitive galvanometer, used in the simple circuit shown in Fig. 8.7 (a). (A protective resistance of 50,000 Ω should be connected in series with a gas-filled cell.) Since emission photocells have a very high internal resistance (e.g. $>10^{11}\Omega$), their output can be efficiently amplified by a triode valve. Fig. 8.7 (b) shows the basic circuit. A current of 10^{-9} amp through the photocell will

produce a p.d. of 10^{-2} V across the grid leak R_1 if the latter is $10^7 \Omega$. 10^{-2} V on the grid may change the anode current through the triode by about 15μA and this can be read on a needle instrument. The initial dark current through the valve can be "backed out" by the battery B_5 and rheostat R_2.
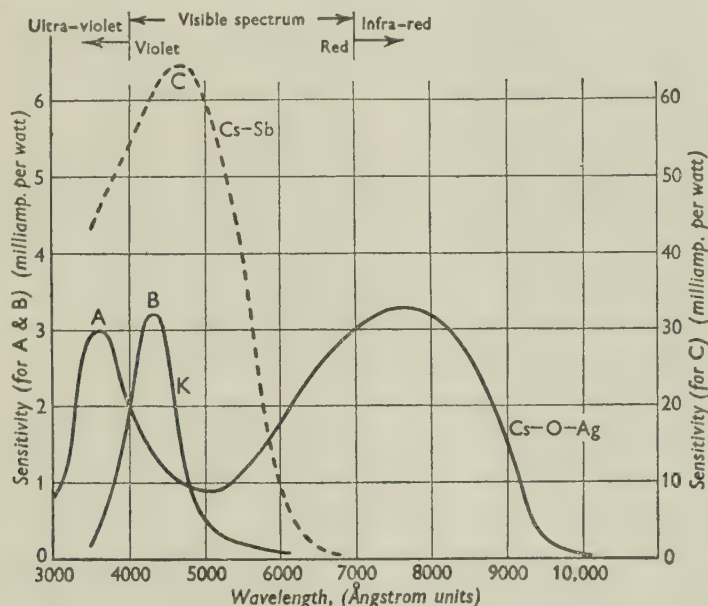
FIG. 8.6. Approximate spectral sensitivity graphs for some emission photocells.
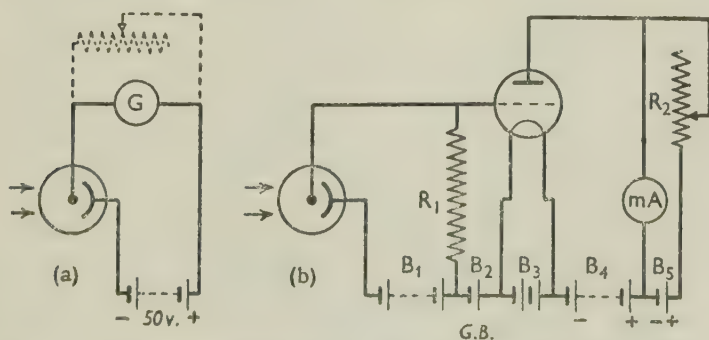
FIG. 8.7. Circuits for measurement of light intensity by means of emission photocells.

(a) Direct measurement of photocell current.   (b) Valve amplification of photocell current.

The circuit shown would be suitable for working a relay from a photocell, but would not normally give linear amplification of the photocell current.   This can be achieved by more complicated circuits, or, alternatively, the valve amplifier can be used as a null-point indicator, and the (linear) change of grid potential produced by the light can be measured with its aid.

The amplification of photocells for measurement of very low light intensities (e.g. for measurement of fluorescence, light-scattering, etc.) requires special methods.[1]   The "photomultiplier" tube is one solution of the problem.[2]

Photo-voltaic cells (also called "barrier layer" or "rectifier" cells). This type of photocell is extremely simple to use as it requires no external battery and generates an e.m.f. when light falls on it; it is also cheap, robust and durable.   The modern form consists of a thin layer of selenium deposited on an iron plate.   The surface of the selenium is coated with a transparent film of metal to collect the electrons released in the surface of the selenium by the absorption of light, and the iron plate constitutes the positive electrode of the cell.

The sensitivity to visible light of selenium photocells (as made, for instance, by Messrs. Evans Electroselenium, Ltd., Bishop's Stortford, England) is about 0.6 μA per ft-candle per sq. cm of sensitive area (or 540 μA/lumen).   The output can therefore be read directly on a needle microammeter if the light intensity is fairly strong or on a robust galvanometer for moderate light intensities. It is a characteristic of this type of cell that the *current* which flows *when the cell is short-circuited* is directly proportional to the light intensity up to several hundred ft-candles.   The open-circuit voltage is *not* linear with intensity (presumably because space-charges are set up).   Consequently, if linear response is wanted, the current-indicating meter should be of low resistance—preferably less than 100 ohms.   With a given external resistance, the proportionality between current and intensity holds more accurately the lower the intensity range.   This type of photocell is not suited to valve amplification, and is therefore not used for very low light intensities.

The relative spectral response of "EEL" selenium cells is shown in Fig. 8.8; it is seen to be rather similar to that of the human eye. The energy distribution in the light of a tungsten filament lamp is also shown.   Modern cells are practically free from "fatigue" and from disturbance by infra-red (heat) rays.

The above characteristics of selenium photocells make them ideally suited for use in chemical "colorimeters".   Fig. 8.9 shows a typical instrument of this type.   Broad spectral ranges selected by means of

glass filters (or a simple monochromator) can be employed and sufficient light is then available to give full-scale deflection on a robust taut-suspension "spot" galvanometer. Given a steady light source, light absorption by solutions can be measured with an accuracy of 1% by this very simple means. Some "absorptiometers"
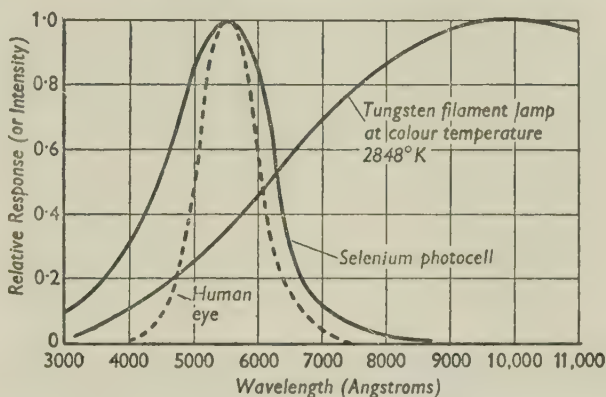
FIG. 8.8. Spectral distribution of response of a selenium photocell compared with that of the human eye, and the spectral distribution of intensity of light emitted from a tungsten filament lamp.
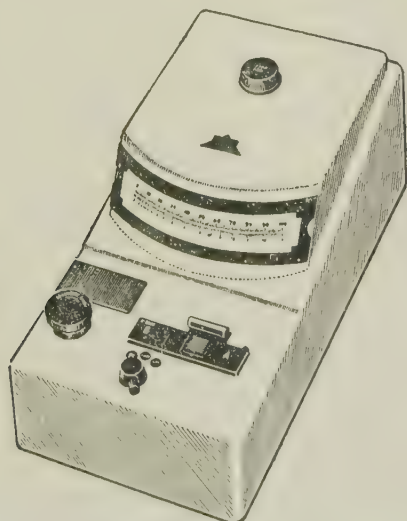
FIG. 8.9. Chemical absorptiometer ("colorimeter") employing a selenium photocell.
(Courtesy Messrs. Unicam Instruments (Cambridge) Ltd., Cambridge.)

employ two similar cells in opposition, and various compensating circuits have also been used. Some gain in stability and range is thus obtained at the expense of simplicity. Selenium photocells can be used similarly to measure turbidity of suspensions, fluorescence, reflectivity, brightness of incandescent bodies, etc.

Photocell-galvanometer amplifiers. An interesting application of photocells in the laboratory is to the *linear* amplification of very small d.c. currents—a problem presenting many difficulties by ordinary electronic methods. In this method the current is used to produce a small deflection of a primary galvanometer which throws a rectangular light spot on to a photocell. The greater the deflection, the more light falls on the photocell and hence the greater the photocell current. By using a divided selenium cell, the two sides being connected in opposition, the sensitivity is doubled and exceedingly small deflections of the primary galvanometer can be measured.

Amplification by photocell is similarly employed, for example, in the commercial recording polarograph of Messrs. H. Tinsley (London).

EXPERIMENT

(*A*) *Investigate the characteristics of a selenium photocell, and* (*B*) *determine the effect of concentration on the absorption of red light by methylene blue solution, using a simple photocell "colorimeter".*

Procedure. (Part A.) Set up the apparatus shown in Fig. 8.10 (a). S is a 6- or 12-V car headlamp bulb, run from an accumulator of large capacity or a constant-voltage transformer. C is the selenium photocell properly mounted, G is a "spot" galvanometer of internal resistance not exceeding 100 ohms. G should preferably be of high sensitivity. R_1 is a variable shunt for reducing the sensitivity of the galvanometer, and R_2 is for changing the resistance of the external circuit. R_1 and R_2 are preferably standard resistance boxes. The apparatus must be set up in a darkened room, or, failing that, the photocell can be mounted at one end of a long rectangular box provided with means for moving the lamp along it, and blackened inside. Only direct light from the lamp must fall on the photocell.

Study the galvanometer deflection (at fixed sensitivity) with different distances, L, between lamp and cell. Make tests of the reproducibility of the readings (including the galvanometer "zero"), and ascertain whether the cell shows "fatigue" on long illumination. Investigate the effect of external circuit resistance on the current-intensity relationship.

Results. (Part A.) Assuming that the light intensity falling on the cell obeys the inverse square law, and that the lamp produces about 1 candlepower per watt, report the results in the form of graphs showing the sensitivity in microamperes per lumen, as a function of light intensity in

foot-candles, at various values of the external circuit resistance. Hence deduce the conditions under which the cell gives a "linear" response to light.

Procedure. (Part B.) A commercial photoelectric colorimeter such as that shown in Fig. 8.9 may be used, but the equivalent arrangement can be readily assembled as shown in Fig. 8.10 (b), either temporarily set up in a dark room, or mounted permanently in a blackened wooden box. Between the lamp S and photocell C are mounted an adjustable aperture A, a condensing lens B, a filter F, a pair of interchangeable glass cells α and β, and an aperture H to exclude stray light. A shutter Z is useful for cutting off the light
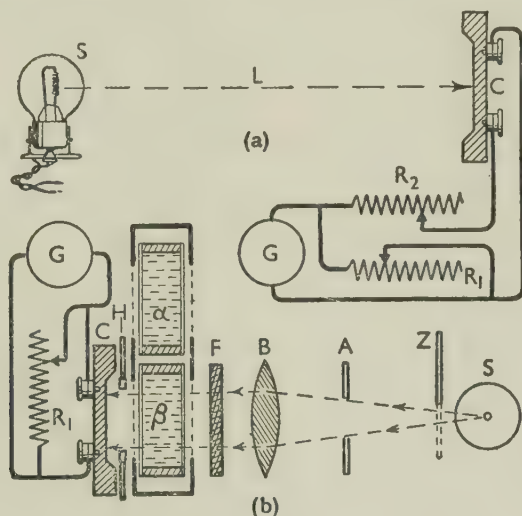
FIG. 8.10. Use of barrier-layer photocells.
(a) Investigation of characteristics of a cell.
(b) Arrangement for absorptiometry.

entirely to check the zero of the galvanometer. A can be an iris diaphragm, precision adjustable slit, hinged V-shaped slit of adjustable angle, or simply a small strip of thin metal which can be turned on a vertical axis in front of a rectangular opening of the same size in a fixed screen. The essential function of A is to provide a smooth control of the amount of light incident on the photocell. Lens B is placed at its focal distance from the filament of S to provide a roughly parallel beam; some colorimeters dispense with it and use divergent light. A number of filters F of different colour are desirable for colorimetry. The cells α and β are of optical quality and accurate dimensions. Rectangular cells of 1 cm path length are most

convenient. They must be mounted on a sliding carriage so that they can be interchanged instantly. Cell α contains pure solvent (water) and cell β the coloured solution.

With cell α in position in front of the photocell, A and R_1, if necessary, are adjusted to produce *exactly* full-scale deflection on the galvanometer. Cell β is then slid into place instead of α, and the new deflection on the galvanometer is observed. These measurements are repeated and the galvanometer zero is checked. The percentage transmission is then given by $100 \times$ (deflection for cell β)/ (deflection for cell α).

When using a "colorimeter" for measuring the concentration of a coloured substance one should employ a filter which transmits light of a wavelength which is strongly absorbed by the substance. Thus, a red filter might be used for a blue dye and vice versa.

This method of colorimetry should clearly be restricted to solutions which transmit between, say, 90% and 10% of the incident light, otherwise the accuracy suffers. Improved accuracy on strongly coloured solutions can often be achieved by standardizing the sensitivity with a standard solution of the substance in cell α instead of pure solvent, thus permitting a higher light intensity (or galvanometer sensitivity) to be used.

Results. If the source were truly monochromatic, the photocell response accurately linear, and Beer's Law were followed by the coloured substance, one should find optical density $(= \log I_0/I) \propto$ (concentration) (p. 160). Glass filters, however, transmit a considerable range of wavelengths; the intensity of the light source in these wavelengths and the spectral sensitivity of the photocell must also be considered. Consideration of these factors shows that the response observed in a simple colorimeter may well deviate from the ideal law. Therefore it is usual in colorimetric analysis to construct an empirical calibration curve of density against concentration, using solutions of known concentration, and then to use the curve subsequently for unknown solutions. This procedure also eliminates the necessity for having accurately linear photocell response; only a reproducible response is needed.

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8E. REFRACTOMETRY

Refractive index: the critical angle principle. When a ray of monochromatic light passes from a less dense to a more dense medium, it is bent or refracted towards the normal. Thus, in Fig. 8.11 (a) if I is the less dense and II the more dense medium, a ray of

light passing from *I* to *II* will be bent so that the angle of refraction *e* will be less than the angle of incidence *i*; and, according to the law of refraction, the relation between these two angles will be such that

$$\sin i / \sin e = N/n$$

where *n* is the index of refraction of the less dense, and *N* the index of refraction of the more dense medium. As the angle *i* increases, the angle *e* also increases, and reaches its maximum value *e'* when *i* becomes equal to a right angle; that is, when the incident light is horizontal. Since $\sin 90° = 1$, the above equation becomes $1/\sin e'$ = N/n, or $\sin e' = n/N$. (If *i* > 90° the ray is totally internally reflected.)

If, therefore, a narrow source of light (*S*, Fig. 8.11 (b)) is placed on the interface between *I* and *II*, and is observed by means of an eyepiece *E* which can turn about the point *O*, one observes a band of light due to rays such as *a* and *b*, leading to a sharp edge, corresponding to the critical ray *c*, and then a region of darkness. The position of the sharp edge gives the critical angle, *e'*. Most instruments for measuring refractive index (*refractometers*) employ this *critical angle principle*.
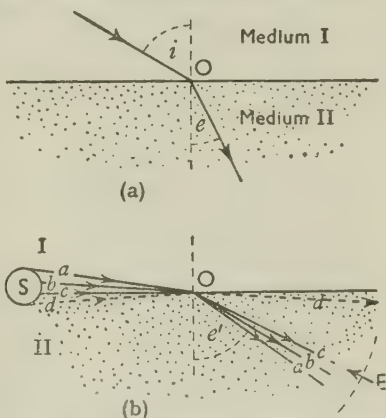
FIG. 8.11. Refraction and the critical angle principle (see text).

Specific and molecular refractivity. Whereas the refractive index *n* of a substance varies with the temperature, the expression $\dfrac{n^2-1}{n^2+2} \cdot \dfrac{1}{d}$ (Lorentz and Lorenz), where *d* is the density, remains nearly constant at different temperatures. The value of this expression is, therefore, dependent only on the nature of the substance, and is a characteristic of it. It is called the *specific refractive power* or *refractivity* of the substance. If the refractivity is multiplied by the molecular weight of the substance, one obtains the *molecular refractivity*, $[R] = \dfrac{n^2-1}{n^2+2} \cdot \dfrac{M}{d}$, where *M* is the molecular weight. [R] has the dimensions of a volume.

Refractivity and polarizibility. Refraction arises from the fact that the extra-nuclear electrons of atoms tend to follow the oscillations of the electro-magnetic field associated with light. It can be shown that, for a

particular frequency of the light $[R] = 4\pi N\alpha/3$ (Clausius-Mosotti equation), where N is Avogadro's number and α is the *electronic polarizibility* of a molecule of the medium, that is to say, the value of the instantaneous dipole moment induced in the molecule when it is placed in an electric field of unit intensity. α is therefore a measure of the 'looseness" of binding of the electrons. It is understandable that the polarizibility (and therefore, refractivity) of a molecule is approximately the sum of the polarizibilities (or refractivities) of its constituent atoms, since the electronic condition of a given element is very similar in its different compounds. Tables of *atomic refractivities* $[r]$ have therefore been prepared from which one can calculate molecular refractivities with fair accuracy. These tables include values for double and triple bonds to be added to the atomic refractivities for compounds containing such bonds; these corrections are needed because multiple bonds are more polarizible than single bonds. Refractivities depend on the wavelength of light employed. The accompanying short list gives atomic refractivities $[r]_D$ for the Na–D line.

Element	$[r]_D$	Element	$[r]_D$
C (singly bonded)	2·418	Cl	5·967
H	1·100	Br	8·865
O (in OH group)	1·525	I	13·900
O (in ethers)	1·643	Double bond	1·733
O (in CO group)	2·211	Triple bond	2·398

The Abbe refractometer. This instrument is the refractometer most commonly used in chemical laboratories. The principle of operation is illustrated diagrammatically in Fig. 8.12 (a), and the appearance of the instrument, as made by Messrs. Bellingham and Stanley (London), is shown in Fig. 8.12 (b).

The optical system consists of three parts—a mirror M, a prism-box PQ which can be rotated as a whole by means of a milled knob R, and a *fixed* telescope, T.

Light from a source S (a pearl lamp or sunlight) is cast by means of the mirror on to the lower prism Q, thus illuminating the upper face of this prism. This face is ground so that it acts as a diffusing screen and provides rays in every direction. The narrow space between the lower (illuminating) prism Q and the upper (refracting) prism P contains a small quantity of the liquid under examination. This liquid must have a refractive index lower than that of the glass of prism P, so that the critical angle phenomenon (explained on p. 171) can be observed. Then, on looking through the telescope, one sees a band of light due to rays which pass obliquely through the liquid. This band finishes sharply, the edge of the light band corresponding to rays which pass through the prism face AB at grazing incidence, thus entering the prism at the critical angle e'.

Now $\sin e' = n/N$ (p. 171), where n and N are the refractive indices of the liquid and the prism respectively. It is readily shown that the angle, α, at which the critical ray emerges from the face AC of the prism is related to n by the equation

$$n = \sin \widehat{BAC}\sqrt{N^2 - \sin^2 \alpha} - \cos \widehat{BAC} \cdot \sin \alpha$$

In practice the telescope is fixed but the prism box is rotated until the critical ray is seen to coincide with cross-wires set in the telescope. Each setting of the prism thus corresponds to a definite critical angle and therefore a definite value of n and this can be read off directly on an engraved scale Z by means of the eyepiece O which moves on an
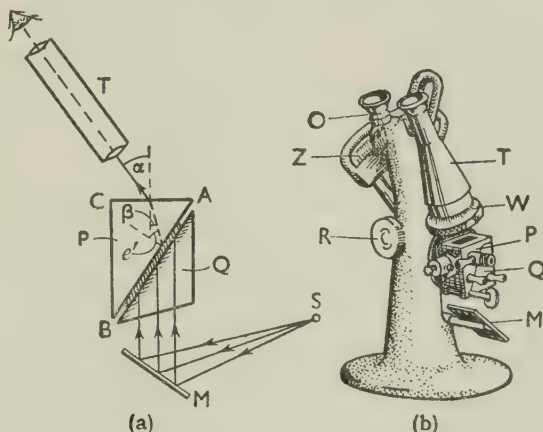
FIG. 8.12. The Abbe refractometer.
(a) Optical principle.
(b) General view of the instrument.
(Courtesy Messrs. Bellingham and Stanley, Ltd., London.)

arm rigidly coupled to the prism box. The instrument requires only a few drops of liquid, and the refractive index can be read very quickly. The usual prism covers the range 1·30 to 1·70 with an accuracy of ±0·0002.

Procedure. In order to carry out a determination of the refractive index of a liquid, open the prism box and place a few drops of the liquid on the ground surface of the lower prism. Close and fasten the prism box again, taking care (by tilting the refractometer forward a little, if necessary) that the liquid does not flow away. A film of liquid will thus be enclosed between the two prisms. Focus the cross-wires of the telescope by rotating the eyepiece and adjust the mirror so as to get good illumination. By means of the knob R, turn the prism box slowly backwards and forwards until the field of

view becomes partly light and partly dark. When white light is used the edge of the light band will show a coloured fringe. By means of the milled ring W on the telescope, rotate the "compensator" (consisting of two prisms, which rotate in opposite directions, and so form a system of variable dispersion) until the coloured fringe disappears and the light-band shows a sharp edge. Now rotate the prism box until this sharp edge is in coincidence with the intersection of the cross-wires in the telescope, and read off directly the index of refraction on the scale through eyepiece O. The third decimal place in the refractive index can be read directly, and the fourth can be estimated with an accuracy of about $\pm0\cdot0002$.

For the purposes of temperature regulation the prisms are enclosed in a metal jacket through which water from a thermostat can be circulated. Before circulating the water, the thermometer must be screwed into place. The temperature of the liquid should be controlled within $0\cdot5°$. The effect of temperature on the calibration of the instrument is small—about $0\cdot0001$ per $15°$.

The scale S gives values for the refractive index for the D line (n_D). Connected with the compensator, however, there is a divided circle, and by reading the number on this dispersion circle, after the light-band in the telescope has been made sharp and free from colour fringe, the value of the dispersion, n_F-n_C, can be calculated from tables supplied with the instrument.

Adjustment of the refractometer. It may be necessary, from time to time, to adjust the setting of the refractometer, and for this purpose a standard glass test-piece is provided, the index of refraction of which is marked on the glass. Open the prism box until the lower prism can be slipped off its hinge. By means of a drop of monobromonaphthalene applied to the polished surface of the test-piece, fix the latter on the surface of the upper prism, the ground edge of the test-piece being directed towards the mirror. Excess of the monobromonaphthalene is to be avoided. Turn the lever so that the reading on the divided arc corresponds with the refractive index of the glass test-piece, and by means of the compensator obtain a sharp band of light, without colour fringe, in the telescope. If this edge coincides with the intersection of the cross-wires, then the instrument is in proper adjustment; but if not, turn the small, square-cut pin at the back of the telescope by means of the special key until coincidence occurs.

The immersion refractometer. When comparatively large quantities of material are available, the dipping or immersion refractometer may be used (Fig. 8.13). In this instrument, the optical principle of which is the same as that of the Abbe refractometer, the prism is rigidly fixed in the telescope tube, in which also there are contained a compensating prism (as in the Abbe apparatus) and a scale. In use, the refractometer is suspended so that the prism dips

into the liquid to be investigated, which is contained in a beaker immersed in a thermostat, regulated to a temperature of 17·5°, the temperature for which the instrument is calibrated. White light is reflected by means of a mirror placed below the beaker, and the sharp edge of the band of light is read off on the scale. In order that fractions of a scale division may be determined with greater accuracy, there is a fine adjustment screw, with graduated drum, by means of which the scale can be moved. At the beginning of the determination, this micrometer screw should be placed in the zero position, and if the edge of the light-band does not coincide with a scale division, the drum is rotated until coincidence occurs. From the graduation on the drum, the fraction of a division through which the scale has been moved can be read off. The position of the edge of the light-band having been determined, the scale reading can be converted to refractive index value by means of the table provided with the instrument. The refractive indices are for the Na–D line. The prism usually supplied is suitable chiefly for aqueous solutions with a refractive index between, say, 1·325 and 1·366. Interchangeable prisms, however, are also made so that the range of refractive indices for which the instrument can be used is extended. By reading to 1 drum division, refractive indices can be measured to 0·00004.

Before use, the adjustment of the instrument must first be tested with water at 17·5°. If the edge of the light-band does not coincide with the appropriate scale division, then the change of micrometer reading needed to make it do so must be determined and this quantity must subsequently be applied as a correction to other readings.

Fig. 8.13. The immersion refractometer.

(Courtesy Messrs. Bellingham and Stanley, Ltd., London.)

The Pulfrich refractometer. This instrument is less used than the Abbe refractometer, but is important for its great accuracy (± 0.00002). The critical angle is observed by means of a right-angled prism (refractive index N) (Fig. 8.14) which carries a glass ring cell cemented to its upper surface to contain the liquid (refractive index n). The prism is fixed. The observation telescope bearing cross-wires rotates about an axis through the point O, and permits the angle of emergence, i, of the critical ray from the side of the prism to be determined on a scale S. The theory is as explained on p. 171, and it readily follows that $n = \sqrt{(N^2 - \sin^2 i)}$. Tables of n corresponding to the measured angle, i, are supplied by the makers

for each prism.   As N is a function of the wavelength concerned, the tables are provided for a number of different wavelengths.   A prism with N about 1·6 is suitable for liquids of $n = 1·3$ to 1·5, and another prism of $N = 1·7$ extends to the range from 1·5 to 1·7.
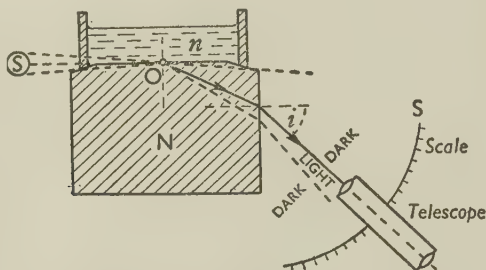
FIG. 8.14. Principle of the Pulfrich refractometer (see text).
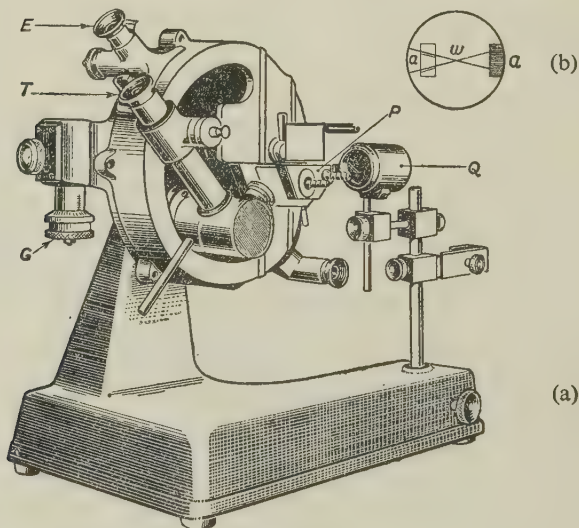
FIG. 8.15. The Pulfrich refractometer.
(a) A modern form of the instrument.   (b) Field of view (see text).
(Courtesy Messrs. Bellingham and Stanley, Ltd., London.)

Details.   Fig. 8.15 (a) shows a contemporary form of the Pulfrich refractometer (as made by Messrs. Bellingham and Stanley, London).   This model is an improvement on the more conventional design, but the manipulations are essentially the same.

As light source one must use a discharge tube or lamp (e.g. Na, H_2, Hg

or Cd lamp) giving well-separated lines (pp. 149- 51). The source is aligned with the upper surface of the prism *P* and placed at a short distance from a lens *Q* which concentrates the light into the required region. Water from a thermostat is circulated round the prism housing. If the full accuracy of the instrument is to be obtained, the temperature of the liquid sample must be controlled to $\pm 0.05°$.

The observation telescope *T* is mounted on a vertical turntable carrying an accurate angular scale which is read by means of the eyepiece *E*. The scale is graduated directly to 15 minutes, and, by means of a micrometer screw and divided drum, head readings can be repeated to 5 seconds. (In older models the scale was divided into degrees and half-degrees (30 minutes), and a vernier, read with a lens, permitted readings to be taken to the nearest minute.) An essential detail, of course, is a screw by which the position of the telescope can be adjusted with the corresponding accuracy.

Determination of the zero point. Before proceeding to make a measurement, the correction for zero, if any, must first be ascertained. This is done with the help of a small right-angled prism let into the side of the telescope tube near the eyepiece. The disc is first of all rotated until its zero coincides approximately with the zero of the scale, and is fixed in this position by means of the screw. A source of illumination (best, a small electric lamp or "torch") is then fixed opposite to the prism. (In the instrument illustrated, the light source is built in.) On looking through the eyepiece of the telescope, the field of view will have the appearance shown in Fig. 8.15 (b). To the right is seen the prism *a*, while to the left of the field of view is seen a bright rectangular patch, *a'*, crossed by two lines running parallel to the cross-wires *w*. This bright patch is the image of the prism *a* reflected from the face of the refracting prism (*P*), and the two marks are the images of the cross-wires. The zero of the instrument is given when the cross-wires *w* coincide with their images. The adjustment to coincidence is carried out by means of the fine adjustment screw *G*, and the point on the scale opposite to the zero of the vernier is then read. This is the zero of the instrument, and the difference of this reading from the zero mark is the correction which has to be applied to each subsequent reading of the scale.

It happens, however, not infrequently, that the prism *P* is slightly turned in its bed, so that the image of the prism and cross-wires is thrown either nearer to or farther from the centre of the field of view. In this case, simultaneous coincidence of both the cross-wires with their images cannot be obtained. The zero is determined, in such a case, by setting the upper cross-wire in coincidence with the upper image, then the lower cross-wire in coincidence with the lower image, and taking the mean of the two readings.

Having ascertained the zero correction, one may now proceed to make measurements of the refractive index by moving the telescope until the cross-wires coincide with the edge of the band of light refracted through the prism.

Other refractometers

The Hilger-Chance refractometer. This recent instrument is of special interest as being a high-precision refractometer which does not employ the customary critical angle principle. Instead, the refraction produced by a right-angle prism of the material is measured by what is in effect, a goniometer arranged in a vertical plane. The means provided for measuring the angular deviation of the ray are extremely refined: a main scale divided in intervals of 10 minutes is supplemented by a micrometer scale reading to 3 seconds. An accuracy of 0.00001 in the refractive index is obtainable over the range 1.30 to 1.95.

This instrument was originally designed for measurement of the refractive indices of optical glasses, but it is readily adaptable to liquids, 2–3 ml being required. Naturally, the full precision of the instrument is not obtainable without exceptionally good temperature control.

Gases: Rayleigh interference refractometer. The principle of the interferometer was adopted by Lord Rayleigh (1896) for measurement of the refractive indices of gases. A beam of light is divided into two parts which pass through two similar parallel slits and then, after traversing similar cells, are brought together to produce interference bands. Any change in the refractive index of the medium in one of the cells (e.g., if a gas is introduced instead of vacuum) causes a displacement of the bands which can be measured by adjusting a tilted compensating glass plate placed in one of the beams. A movement of one-fortieth of a band can be detected, corresponding to a refractive index difference of 2×10^{-8}. The method is therefore particularly suitable for detecting small changes of gas composition; for instance, 0.01% of hydrogen in air can be detected. The instrument can also be adopted for measurements with liquids; again, it provides an exceptionally sensitive method of measuring small changes of refractive index, and, hence, of composition.[1]

Differential refractometers. The modern method of molecular weight determination based on the scattering of light requires a knowledge of the refractive index of the solute particles.[2] This can be obtained from measurements of the refractive indices of solutions of different concentration, and several simple differential refractometers have been developed especially for this purpose.[3]

Refractometric determination of the composition of solutions. Refractometric measurements may be used, very advantageously, for the quantitative determination of the composition of binary solutions. For this purpose, the refractive indices of a series of solutions of known composition are first determined (e.g. by means of the Abbe or immersion refractometer), and the values so obtained are plotted on a graph. The composition of an unknown solution can then be ascertained from the graph after the index of refraction of the solution has been determined. The relation between refractive index and composition for a large number of solutions is given in the International Critical Tables (Vol. VII).

The composition of a *dilute* solution of two liquids can be calcu-

lated approximately from the refractive index of the solution provided one knows the refractive indices and densities of the two components. If n_1 and n_2 are the refractive indices of the two components, and n_3 the refractive index of the solution, and if d_1, d_2, and d_3 are the corresponding densities, the percentage amount p, of component " 1 " can be calculated approximately by means of the expression,

$$\frac{n_1-1}{d_1} \cdot p = 100 \cdot \frac{n_3-1}{d_3} - \frac{n_2-1}{d_2}(100-p)$$

The refractive index of a solution, calculated by means of this expression, should be compared with that determined directly.

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8F. POLARIMETRY

When ordinary light is passed through a Nicol prism (made from Iceland spar), the emergent light is plane-polarized, that is, the electromagnetic vibrations take place in one plane. If this polarized light is now examined by means of another Nicol prism, it will be found that, on rotating the latter, the field of view appears alternately light and dark, the minimum of brightness following the maximum as the prism is rotated through an angle of 90°. The prism by which the light is polarized is called the polarizer, and the second prism, by which the light is examined, is called the analyzer.

If, when the field of view appears dark (which occurs when the axes of the two prisms are at right angles to each other), a tube containing a solution of cane sugar is placed between the two prisms, the field lights up, and one of the prisms must be turned through a certain angle, α, before the field becomes dark again. The solution of cane sugar has therefore the power of turning or rotating the plane of polarized light through a certain angle, and is hence said to be *optically active*. When, in order to obtain darkness, the analyzer has to be turned to the right, i.e. clockwise, the optically active substance is said to be *dextro-rotatory*, and *laevo-rotatory* when the analyzer must be turned to the left.

It will, of course, be possible to obtain a position in which the field of view becomes dark by rotation of the analyzer either to the right or the left, because in one complete rotation of the prism through

360°, there are two positions of the analyzer, 180° apart, at which the field is dark, and similarly, two positions at which there is a maximum of brightness. In determining the sign of the activity of a substance, one takes the direction in which the rotation required to give extinction is less than 90°.

The angle of rotation depends on (1) the nature of the substance, (2) the length of the layer through which the light passes, (3) the wavelength of the light employed (the shorter the wavelength, the greater the angle of rotation), (4) the temperature. In order, therefore, to obtain a measure of the rotatory power of a substance, these factors must be taken into account, and one then obtains the *specific rotation*. This is defined as the angle of rotation produced by a liquid which in the volume of 1 ml contains 1 g of active substance, when the length of the column through which the light passes is 1 dcm. The specific rotation is represented by $[\alpha]$, the observed angle of rotation being represented simply by α.

With a pure active liquid, the specific rotation is obtained from

$$[\alpha] = \frac{\alpha}{l \cdot d}$$

where l is the length of the column of liquid in decimetres, and d is the density. If account is taken also of the other factors on which the rotation depends, viz. temperature and wavelength of light, a number is obtained which, for the particular conditions of experiment, is a constant, characteristic of the substance. Thus, $[\alpha]_D^{25°}$ represents the specific rotation for the D line (sodium light) at the temperature of 25°.

When the active substance is examined in solution, the concentration must be taken into account, in accordance with the expressions:

$$[\alpha] = \frac{100\alpha}{lc}, \text{ or } [\alpha] = \frac{100\alpha}{lpd}$$

where c is the number of grams of active substance in 100 ml of solution, p is the number of grams of active substance in 100 g of solution, and d is the density of the solution. In expressing the specific rotation of a substance in solution, the concentration and the solvent (which also has an influence on the rotation) must be stated.

The polarimeter. The arrangement of the optical parts of the Lippich polarimeter, the type now generally adopted, is shown diagrammatically in Fig. 8.16 (a).

Monochromatic light from the source L passes through the lens A, which renders the rays of light parallel, and then through the polarizing prism B. It then passes through the observation tube O, and thence through the analyzer D. The field of view is observed

through the telescope *EF*. At *C* there is a small Nicol prism which covers half of the opening at the end of the polarizer tube. The light on passing through this prism is altered in phase by half a wavelength, but still remains plane-polarized. In this way, two beams of polarized light are obtained; and if the polarizer is rotated so that the plane of polarization forms an angle (δ) with the optical axis of the Nicol prism, the planes of polarization will also be inclined at an angle, equal to 2δ. This is the half-shadow angle. On rotating the analyzer, a position will be found at which the one beam will be completely, the other only partially, extinguished. The one half of the field of view, therefore, will appear dark, while the other half will still remain light (as shown by (A) in Fig. 8.16 (b)). On rotating the analyzer still further through the angle 2δ, a second position, (B), will be found at which the second beam will be extinguished, while the first is no longer so. In this position of the analyzer, the half of the field which was formerly bright will now be
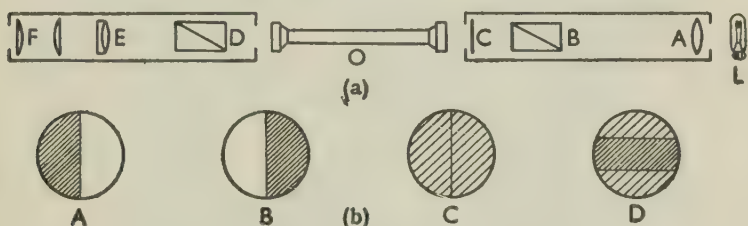
FIG. 8.16. Principle of the polarimeter.
(a) Arrangement of the optical system. (b) Appearance of the field of view.

dark, and that formerly dark will now be light. When, however, the analyzer occupies an intermediate position (C), the field of view will appear of uniform brightness; and this is the position to which the analyzer must be set. Many polarimeters give a triple field, (D), and this arrangement facilitates matching, especially if the illumination of the field of view is not perfectly uniform.

By diminishing the angle δ (by rotating the polarizer) the sensitiveness of the instrument can be increased, because now the angle 2δ, through which the analyzer must be rotated in order to cause the shadow to pass from one half to the other of the field of view, is diminished. By diminishing the angle of half-shadow, however, the uniform illumination of the field of view is also diminished, so that the increased sensitiveness due to diminution of the angle of half-shadow is partly counteracted by the greater difficulty in deciding when the field is uniformly illuminated, unless the light intensity of the source can at the same time be increased. With a source of light of given intensity, therefore, the angle of the half-shadow must

be fixed so that the determination of the position of uniform illumination can be made without unduly straining the eyesight.

The visual matching of the two beams can be made more accurately if the eye is dark adapted; either the polarimeter should be used in a darkened room or the observer should use a black cloth to exclude extraneous light. As with all optical instruments, eyestrain is reduced if the observer can be comfortably seated and can look into the eyepiece without stretching.

The complete polarimeter is shown in Fig. 8.17. At the end S, which is directed towards the source of light, are the lens and the light-filter, consisting either of a solution of potassium dichromate
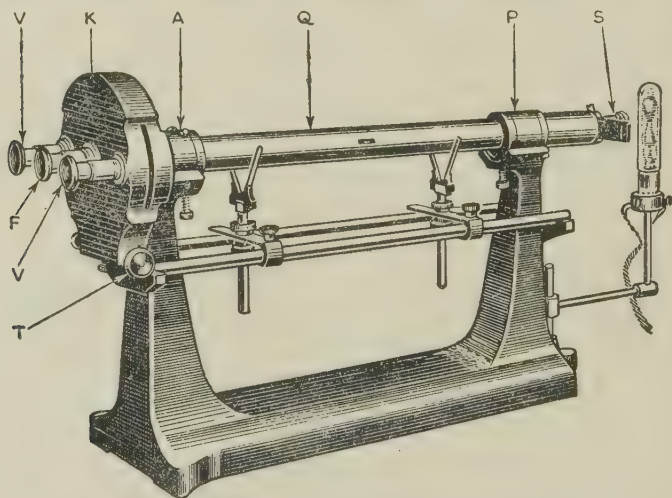
Fig. 8.17. Standard form of polarimeter.
(Courtesy Messrs. Bellingham and Stanley, Ltd., London.)

or an equivalent gelatine filter. The polarizing prism is at P. In most polarimeters there is a lever and scale by means of which the angle of half-shadow can be altered. The observation tube is placed in a trough in the middle part of the instrument, Q, and is protected from extraneous light by a cover. The analyzer is in the portion of the tube at A. F is the telescope with eyepiece. K contains a graduated disc, which can be caused to rotate, along with the analyzer, past fixed verniers situated on opposite sides of F by means of a slow-motion screw. The two sides of the scale are read to $0 \cdot 01°$ by the verniers with the assistance of a magnifying eyepiece, V. In the polarimeter made by Messrs. Hilger and Watts, Ltd. (London), verniers have been replaced by a direct-reading eyepiece scale.

A small polarimeter employing the sheet polarizing material "Polaroid" in place of Nicol prisms is made by Messrs. Hilger and Watts Ltd. (Fig. 8.18.) This permits simplification of design while sufficient accuracy for many purposes (e.g. sugar determination) is retained. The model shown is easily readable to 0·05° on a simple glass scale graduated in 0·1° divisions.

Polarimeters intended specifically for the determination of the concentration of sucrose are termed saccharimeters; they are often provided with a scale graduated in terms of sugar concentration.
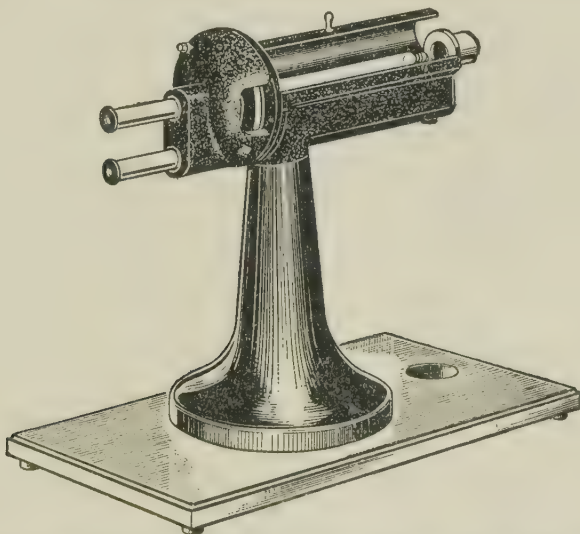
FIG. 8.18. Simplified form of polarimeter, employing "Polaroid" sheet. (Courtesy Messrs. Hilger and Watts, Ltd., London.)

Light sources. Sodium laboratory or street-lighting lamps (see p. 150) are generally used for polarimetry. When measurements are needed at other wavelengths, a mercury lamp may be used in conjunction with special filters, or, better, the image can be examined with a spectroscopic eyepiece or the instrument can be combined with a monochromatic illuminator (e.g. the wavelength spectrometer, p. 153).

Polarimeter tubes. The observation tube for containing the liquid generally consists of a tube of thick glass with accurately ground ends which are closed by means of circular plates of optical glass. These are held in position by screw-caps with rubber washers (Fig. 8.19 (a)). The caps must not be screwed down too tightly as strain in the glass may cause spurious polarization. Polarimeter

tubes are generally 10 cm long and about 1 cm diameter, but other sizes are made, including micro-tubes requiring less than 0·5 ml of liquid.

The form of tube shown in Fig. 8.19 (b) has a side opening for filling and a metal jacket through which water from a thermostat can be circulated to control the temperature of the liquid.

Adjustment and use of the polarimeter.   Set up the polarimeter so that the polarizer lens is situated at its focal distance from the sodium lamp—i.e. so that parallel light passes along the section which will be occupied by the polarimeter tube.   The light source should be adjusted to give as uniform an image as possible in the eyepiece. Clean the polarimeter tube, fill it with distilled water and set it in place between polarizer and analyzer.   Focus the eyepiece of the telescope on the line dividing the field of view.   Now determine the "zero-point" of the instrument by rotating the analyzer until the
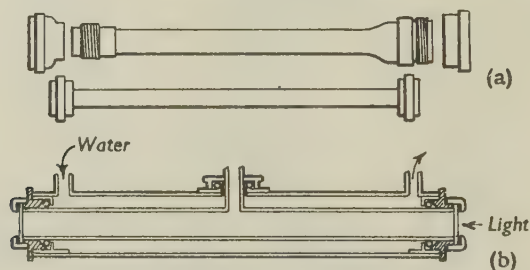
FIG. 8.19. Polarimeter tubes.
(a) Plain tubes.   (b) Water-jacketed tube with side opening.

best match between the parts of the field is obtained.   This position should be approached several times from either side, and readings should be taken on the two verniers (in instruments so fitted), and the mean of the readings taken.   The object of reading both sides of a circular scale, i.e. at points on the graduated circle 180° apart, is to correct for any eccentricity in the construction of the scale.

Since the position of the analyzer required to give equal illumination of the two parts of the field depends on the angle of the half-shadow, the arm which rotates the polarizer must be fixed before the zero point is determined.   Some instruments provide means of setting the scale to 0·00° when the analyzer has been set to the match-point with distilled water in the cell.   With others, the "zero" reading must be taken and subtracted from the results subsequently obtained with optically active solutions to obtain their true rotations.

EXPERIMENT

Determine the specific rotation of sucrose.

Procedure. Prepare three solutions of sucrose by weighing out about 5, 10 and 20 g of pure sucrose, previously dried in a steam oven, dissolving in distilled water, and making up the volumes to 100 ml at the temperature to be used in the determination (say, $20°$ or $25° C$). Water at this temperature must be circulated from a thermostat round the water-jacket of the polarimeter tube. Determine the "zero" with distilled water as described above and then the rotation for each solution in turn in the same way. The tube must, of course, be rinsed several times with portions of the new solution each time the solution is changed. Calculate the specific rotation $[\alpha]_D^t$ from the results, and ascertain whether $[\alpha]$ depends on the concentration.

In place of sucrose, the above experiment may be made with any other optically active substance in an appropriate solvent (e.g. tartaric acid, quinine sulphate, camphor, ethyl malate, etc.) One may verify, also, that the angle of rotation of a given solution is strictly proportional to the path length of the cell employed.

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CHAPTER 9

THERMOCHEMISTRY

Introduction

Most chemical processes are accompanied by a measurable absorption or evolution of heat. It follows from the 1st Law of Thermodynamics that the magnitude of the heat change is proportional to the quantity of substance involved and depends also on the physical state of the reactants and the products, but it is independent of the "path" by which the reaction is brought about. Consequently, to express unambiguously the thermal process accompanying a given reaction, say, $A+B \rightarrow C+D$, one must state the conditions of A, B, C, and D, (e.g. gas, liquid, solid or solution; temperature and, if gaseous, pressure), and indicate the amount of substance for which the value is given, (e.g. one mole of A), and also the sign (endothermic or exothermic).

The heat change accompanying a physical or chemical process is measured by some form of *calorimeter*; the measured rise or fall of temperature multiplied by the total heat capacity of the calorimeter gives the quantity of heat in calories. Many different forms of calorimeter are in use for studying the "heats" of the various types of physical and chemical processes. For example, it is frequently necessary to know *specific heats** (for gases, liquids and solids), *latent heats** (of fusion, evaporation, sublimation and transition), *heats of solution, dilution and mixing*, and *heats of reaction* (including neutralization, combustion, hydrogenation, etc.). In addition, special forms of calorimeter have been designed for measurements at very high or very low temperature, and for special purposes such as determination of heats of adsorption, wetting, etc.

The technique of calorimetry presents two principal difficulties— firstly, how to determine the heat capacity of the calorimeter and all its contents, and, secondly, how to deal with the inevitable exchange of some heat between the calorimeter and its surroundings. The heat capacity can be computed if all the components of the calorimeter and its contents are weighed separately and their specific heats are known. When this method is not applicable the "water equivalent" must be found by supplying a known amount of heat

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* A textbook of practical physics should be consulted for details of calorimeters employed for measuring specific and latent heats.

to the system and determining the rise of temperature which it produces. The heat is best supplied electrically and measured as the product of volts × amps × seconds (joules), but it should be noted that the accuracy of the product will not be high unless the electrical quantities are measured with high precision—say, by a potentiometric method, (p. 247). Other methods of supplying a known number of calories include the "method of mixtures" using a heated body of known specific heat, and by the use of well-established heats of reaction (e.g. neutralization or combustion—cf. p. 188).

There are two ways of dealing with the problem of heat exchange between calorimeter and surroundings. The usual method is to apply a correction to the observed change of temperature. An obvious precaution is to arrange that the correction shall be relatively small and the heat exchange regular; this is the principle of the classical "shielded can" calorimeter. The other solution is the *adiabatic calorimeter* in which the surroundings are automatically maintained at the same temperature as the calorimeter. This eliminates heat exchange entirely, but rather complicated instrumentation is required.[1] For many purposes the heat exchange can be rendered practically negligible by using a Dewar vessel (Thermos flask) as calorimeter. The heat capacity must be measured with a small electrical immersion heater. For endothermic processes one can determine directly how much electrical energy is required to counteract exactly the cooling effect of the process.

The temperature change of the calorimeter must be kept to a few degrees, and consequently sensitive thermometers of the Beckmann type are generally used. Alternatively, platinum resistance thermometers or multiple-junction thermocouples may be employed in work of high precision.[2]

9A. THE CLASSICAL CALORIMETER

Fig. 9.1 shows diagrammatically the most common type of calorimeter, suitable for measurements with liquids and solids in the neighbourhood of room temperature. The central vessel, *A*, is a metal can, usually of silver, having a capacity of at least 500 ml. It is surrounded by one or more polished metal radiation screens, *B*, and finally a water-filled double jacket, *C*, itself enclosed in felt. The various compartments are closed by ebonite lids which are suitably cut to take a Beckmann thermometer, *E*, (provided with a lens, *F*), and a glass or stainless steel stirrer, *G*, preferably driven by a small electric motor, *H*, and guided by a bearing, *J*. The speed of the motor is controlled by an external rheostat. The whole arrangement is intended to minimize heat exchange to or from the vessel *A*,

and, above all, to make such exchange as does occur as regular as possible so that corrections can be applied (see below). The use of the calorimeter will be illustrated for measurements of heats of neutralization and of solution.

EXPERIMENT

Determine the heat of neutralization of hydrochloric acid with sodium hydroxide.

Procedure. Prepare approximately $0.25N$ solutions of hydrochloric acid and of sodium hydroxide, free from carbonate, and determine their concentration by titration.
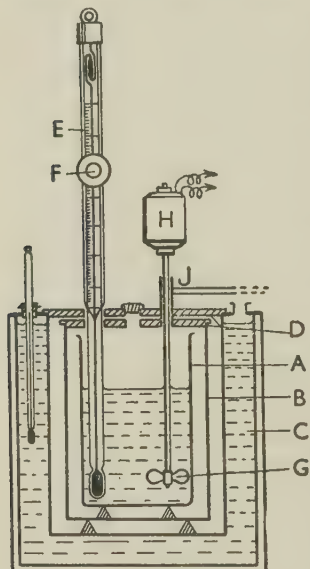
FIG. 9.1. Calorimeter for heats of neutralization, solution, etc.

Fit together the calorimeter as shown in Fig. 9.1, the outer vessel having been filled with water some hours previously in order that it may acquire, as nearly as possible, the temperature of the room. A Beckmann thermometer, previously set (p. 108) so that the mercury stands at the lower end of the scale at the temperature of the room, is passed through the holes in the covers of the calorimeter and supported so that the bulb passes about two-thirds down the calorimeter. 250 ml of the caustic soda solution are placed in the calorimeter, and the stirrer is set in motion at a moderate speed

Meanwhile, 250 ml of the hydrochloric acid solution are placed in a tap funnel which is set up to deliver into the calorimeter. (The funnel may be rinsed previously with acid and drained for one minute to correct for the liquid which adheres to the glass. A trace of wetting agent may also be added.) The funnel is wrapped with felt to minimize temperature fluctuations. The temperature of the acid is read by another Beckmann or calorimeter thermometer. The readings of this thermometer must be compared with those of the thermometer placed in the alkali, to ascertain whether the temperatures of the acid and alkali are the same at the time of mixing, or, if not, what the difference of temperature is.

The temperatures registered by the thermometers immersed in the acid and alkali should be read, say every minute, for at least five minutes before the mixing of the solutions takes place. During this

time the solutions should be stirred quietly. Then, at a particular
moment which must be noted, the acid is run as rapidly as possible
into the alkali, the two solutions mixed well, and the temperature of
the mixture read every half-minute or every minute for five or ten
minutes after mixing took place, until it is found that the fall of
temperature becomes uniform. At first the temperature rises
rapidly, then more slowly, and then begins to fall. As the tempera-
ture rises above that of the room, radiation from the calorimeter is
taking place; it follows that the highest temperature read will be
lower than if no loss of heat by the calorimeter occurred. In order,
therefore, to get the true elevation of temperature produced by the
heat of neutralization, the temperatures read on the thermometer
before and after mixing should be plotted on squared paper, the
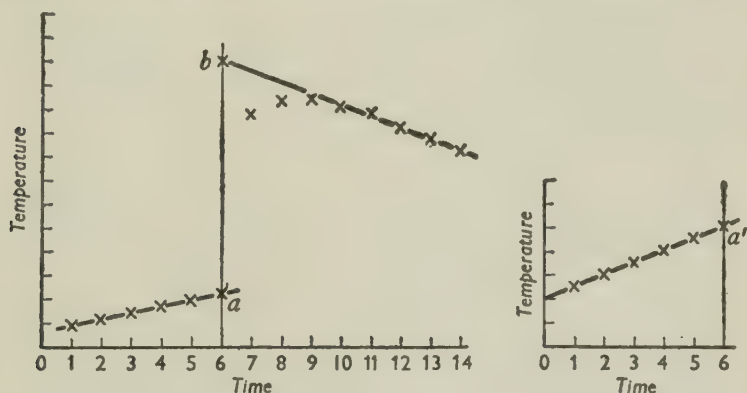
Fig. 9.2. Simple graphical correction for heat exchange in calorimetry.

thermometer readings being represented as ordinates and the time
as abscissae. In this way two graphs similar to those shown in
Fig. 9.2 will be obtained.

In this graph the temperature of acid and alkali is represented as
rising slowly previous to mixing, but the reverse may, of course,
be found. If the time of mixing was, say, at the sixth minute, the
temperature (t_1 or t_1') which the alkali and acid would have at that
moment is obtained by drawing a line through the different tempera-
ture readings and producing it to cut the perpendicular at the sixth
minute (point a or a'); and the highest temperature (t_2) which would
have been reached in the absence of radiation is obtained by drawing
a straight line through the last readings (when the fall of temperature
has become uniform), and producing this line back so as to cut the
perpendicular at the sixth minute. This gives the point b. The

distance ab then gives the elevation of temperature required, $(t_2 - t_1)$.

Calculation of the heat of neutralization. The heat produced in the reaction must be equal to the heat required to raise the solution, the calorimeter, the thermometer, and the stirrer through the range of temperature $t_2 - t_1$ degrees. This, however, is equal to the sum of the masses of the different parts multiplied by their specific heats. For the heat veloved on mixing the acid and alkali, therefore, one has

$$\text{heat evolved} = (m_1 s_1 + m_2 s_2 + m_3 s_3 + m_4 s_4)(t_2 - t_1)$$

where m_1, m_2, m_3, m_4 are the masses of the solution, calorimeter, thermometer, and stirrer respectively, and s_1, s_2, s_3, s_4, their respective specific heats. The following list gives the specific heats of some materials commonly employed in calorimeters; Ag 0·056, Ni 0·109, Cu 0·091, brass 0·089, stainless steel 0·107, glass 0·16.

The specific heat of the solution will vary more or less from that of pure water according to the concentration of the dissolved salt. With solutions of the concentration used above, it will be sufficiently accurate for present purposes to take the water-equivalent of the solution (i.e its mass multiplied by its specific heat), as being equal to that of the *water* contained in it. Otherwise, tables must be consulted.

In the case of the thermometer, which consists of glass and mercury the weight of which cannot be determined separately, the water-equivalent is obtained by making use of the fact that the specific heat of equal *volumes* of glass and mercury is practically the same and equal to 0·47 per ml. To obtain the volume, a beaker of water is counterpoised on the balance, and the thermometer then supported on a stand so that the bulb is immersed in the water. The weight which has now to be added in order to obtain equipoise gives the volume of the bulb. In the case of the Beckmann thermometer the stem above the bulb is not solid, so that the external volume does not represent the volume of the glass and mercury. The external volume of the stem, so far as it was immersed in the solution during the experiment, should be determined separately from that of the bulb, and about one-fifth of the volume so obtained taken as the volume of the glass and mercury. Fortunately, this term is small.

Results. Express the heat of neutralization in kilocalories per gram equivalent.

When a strong acid reacts with a strong base, the reaction is $H^+ + OH^- \rightarrow H_2O$. The heat of reaction is therefore approximately a constant, namely, 13·7 kcal/g equivalent. In practice different acids and alkalis may give appreciably different values on account of (a) incomplete dissociation, and (b) concentration effects. These may be investigated by repeating the experiment, using (a) a weak acid or base, and (b) a concentrated solution of acid or alkali. One may also investigate heats of dilution directly.

Similar experiments may be made with redox reactions, precipitation reactions, etc.

Heats of solution. The heat of solution of a solid or liquid substance can be determined in practically the same manner as that

employed for the determination of the heat of neutralization, and the same apparatus can be employed. Since the heat which is evolved or absorbed on dissolving a substance depends on the amount of water or other solvent employed, the statement of the heat of solution has a definite meaning only when the concentration of the solution formed is given. If the dilution is so great that further dilution is unaccompanied by any heat effect, then the heat measured per mole of solute is known as the heat of solution at infinite dilution. Usually, however, it will not be possible to determine this heat of solution directly, and one must therefore state the number of moles of water in which one mole of solute is dissolved. Further, a clear distinction must be made between the quantity known as the *integral heat of solution* (which is the heat obtained when 1 mole is dissolved in X moles of solvent), and the *differential heat of solution*. The latter is the heat change *per mole of solute* when an infinitesimal amount of substance is dissolved in a large amount of solution of stated concentration. This is the "heat of solution" involved in calculations of the influence of temperature on solubility (p. 136).

EXPERIMENT

Determine the integral heat of solution of potassium nitrate in water.

Procedure. Blow a fragile bulb on the end of a 1 ft length of glass tubing of about 1 cm bore. Dry it, along with a quantity of finely powdered KNO_3, in an oven, and, when cool, weigh about 15 g of the salt into the bulb. Then set up the bulb in the centre of the calorimeter with about 500 g of water (weighed). Set the stirrer going (as fast as permissible without splashing) and take a series of temperature readings as in the previous experiment. When a steady rate of exchange of temperature is attained break the bulb on the bottom of the calorimeter and stir up the contents vigorously. Take temperature-time readings until a steady temperature change is again reached.

Results. Correct the temperature change graphically as before (Fig. 9.2) and compute the heat capacity from the weights. Estimate the proportion of the glass tube which was actually immersed in the calorimeter. The specific heat of KNO_3 solution containing 1 mole per cent of the salt can be taken as 0·943. The accuracy of the experiment depends largely on whether the salt dissolves rapidly. If more than about five minutes are required, the simple extrapolation for heat exchange becomes inadequate (cf p. 196).

In determining the heat of solution of salts attention must be paid not only to the amount of water per mole of salt but also to whether the salt is anhydrous or hydrated. The table on the next page shows that the degree of hydration affects the heat of solution considerably.

The difference between the heats of solution of the anhydrous and the hydrated salt gives, of course, the heat of hydration of the solid.

Salt	Number of moles of water per 1 mole of salt	Heat of solution evolved, kcal per mole
KCl	200	$-4\cdot4$
KNO_3	200	$-8\cdot5$
$ZnSO_4$	400	$+18\cdot5$
$ZnSO_4.7H_2O$	400	$-4\cdot24$
$CuSO_4$	300	$+15\cdot8$
$CuSO_4.5H_2O$	300	$-2\cdot7$

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9B. THE BOMB CALORIMETER

A large number of thermochemical data have been obtained from measurements of *heats of combustion*. These data are not restricted in usefulness to the directly-measured combustion reactions, for by combining several such reactions according to Hess's Law one can deduce the heats of other reactions. For example, *the heat of formation*, ΔH_f, of methane, CH_4, cannot be determined directly, but it can be calculated from measurements of the separate heats of combustion of carbon, hydrogen and methane; thus:

(1) $C+O_2 \rightarrow CO_2$ $: \Delta H_1 = -94,030$ cal

(2) $2H_2+O_2 \rightarrow 2H_2O$ $: \Delta H_2 = -136,636$ cal

(3) $CH_4+2O_2 \rightarrow CO_2+2H_2O$ $: \Delta H_3 = -212,790$ cal

(4) $= (1)+(2)-(3)$ $: \Delta H_4 = \Delta H_1+\Delta H_2-\Delta H_3$
          $C+2H_2 \rightarrow CH_4$ $= -17,876$ cal
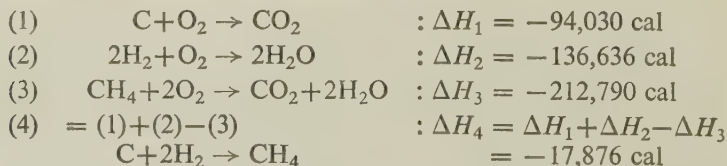
The heat of combustion is best determined by the method due to Berthelot, which consists in burning the substance in an atmosphere of compressed oxygen. The original design of the autoclave in which the combustion takes place (the Berthelot bomb) has been modified in various ways. The form to be described here is the

modification due to Mahler, as made by Messrs. C. W. Cook & Sons, Ltd., Birmingham.

It should be noted that, unlike other calorimeters, a bomb calorimeter measures the heat of a reaction *at constant volume* (instead of at constant pressure). The heat evolved must therefore be identified with the decrease of internal energy, $(-\Delta U)$, rather than of "heat content" $(-\Delta H)$. The relation between the two is $\Delta H = \Delta U + \Delta(PV)$. The volume change of any solids or liquids involved in the reaction can be ignored, and the
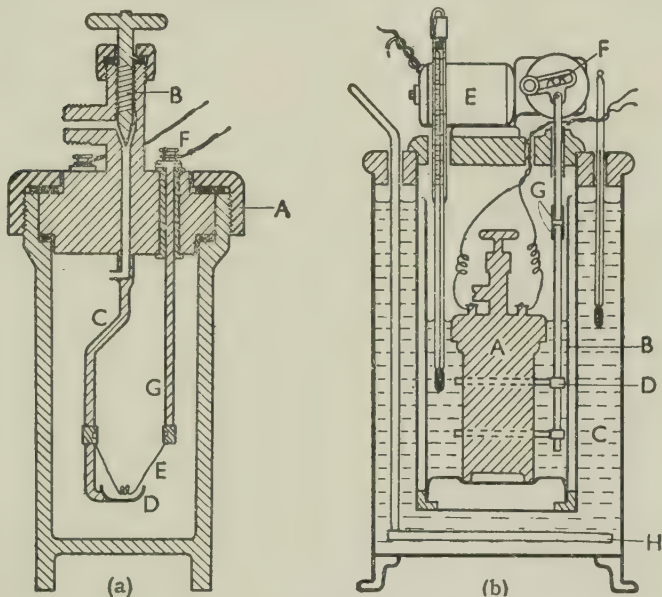
FIG. 9.3. The bomb calorimeter.
(a) Construction of the bomb.   (b) Arrangement of apparatus in the calorimeter.

energy terms $\Delta(PV)$ can be calculated, assuming the ideal gas laws to apply, as equal to ΔnRT, where Δn is the increase of the number of moles of gas during the reaction.

The bomb. The bomb (Fig. 9.3 (a)) consists of a stainless steel pressure vessel about three inches in diameter. The lid is held in place by a strong locking-nut, A, and rendered gas-tight by washers. Oxygen is charged into the bomb through the needle-valve, B. A rod, C, supports a crucible of silica or platinum to contain the substance which is to be burnt. Combustion is initiated by means of a fine platinum or iron wire, E, which is heated momentarily to redness by passage of an electric current, the current being introduced through an insulated terminal, F, and the rod C (which is in electrical connection with the lid).

P.P.C.—13

The calorimeter. Fig. 9.3 (b) shows the rest of the apparatus. The bomb A is placed in water in a copper calorimeter vessel, B, which is surrounded by a double-walled copper water-jacket, C. The water in the inner vessel is stirred automatically by a reciprocating stirrer, D, driven by a small electric motor, E, and reduction gear and eccentric, F. In order to minimize heat conduction along the stirrer, an ebonite rod, G, is interposed between the upper and lower parts. The top of the apparatus is closed by two wooden lids which are provided with holes to take a Beckmann thermometer for the inner vessel, and an ordinary thermometer graduated in tenths of a degree for the outer water-jacket. The latter should be provided with a simple stirrer, H.

The water-equivalent of the calorimeter must be determined by burning a known weight of a substance of well-established heat of combustion. Pure benzoic acid is usually used, its heat of combustion being 6,318 calories per g.[1] As the water-equivalent is about 3,000 g, combustion of 1 g of benzoic acid gives a temperature rise of about 2° C. The same amount of water must, of course, be used in the calorimeter for the experiment with benzoic acid as with the test substance, or allowance must be made.

Procedure. The substance to be burned is first compressed into a pellet, and, after being weighed, is placed in the crucible D. A piece of fine iron wire, about one-tenth of a millimeter in diameter and 6–7 cm in length, is weighed, and its ends connected with the rods C and G. The middle portion of the wire should be formed into a narrow spiral by twisting it round a pin. When the wire is attached, raise the crucible until the middle portion of the iron ignition wire touches the pellet of compressed substance. After having coated the washer and the screw on the bomb with vaseline, the cover is tightly screwed down with the help of a large spanner, the bomb being meanwhile fixed in its holder. Be very careful that no grit gets either on the washer or in the screw of the bomb. The latter is now ready to be filled with oxygen.

A cylinder of compressed oxygen fitted with a needle valve and pressure gauge is connected to the valve B by the metal pipe provided with the calorimeter. Open the valve B slightly, then the main cylinder valve, and then *cautiously* open the slow-release valve attached to the cylinder and allow oxygen to stream slowly into the bomb until the pressure registered on the manometer is 20–25 atm. Now close the valves and disconnect the tube from the bomb. If there is any leakage of gas it will generally be detectable by a slight hissing sound.

The calorimeter may now be prepared. The water-mantle having been filled with water (preferably some hours previously), a thermo-

meter is hung in the air-space inside. After it has taken the temperature of the enclosure, the temperature is read. A Beckmann thermometer is now set (p. 108) so that the lower end of the scale represents a temperature of about 1·5–2 degrees *below* that found in the enclosure of the water-mantle.

The calorimeter vessel is then tared, 2·5 litres of water placed in it, and the weight of the water determined on a balance accurate to about 1 g. The readings of the Beckmann thermometer and the outer-jacket thermometer should be noted when they are at the same temperature in a vessel of water; this is for the "heat-loss correction" (p. 196).

In order to reduce the error due to radiation, the temperature of the water in the calorimeter should be such that, before the combustion in the bomb occurs, it is about as much below the surrounding temperature (temperature of the air-space) as it will be above it after the combustion has taken place. As the rise of temperature should be about 2·5° to 3°, the temperature of the water should be made about 1·5° lower than that of its surroundings.

The charged bomb is lowered cautiously into the water of the calorimeter. Flexible wires are then connected to the terminals, and the lid of the calorimeter placed in position. Insert the thermometer through the cover of the calorimeter and set the stirrer in motion at such a rate that it rises and falls about once per second. After the bomb has been in the water about five minutes, commence reading the temperature on the thermometer, readings being made every minute for about ten minutes. At the tenth minute fire the ignition wire by means of a switch key, in series with the mains and a rheostat—a suitable potential must be found by preliminary experiments. The iron wire will thereby be caused to burn and will ignite the substance in the crucible. The temperature of the water in the calorimeter will now begin to rise rapidly. Again take readings of the temperature, minute by minute (it will probably be impossible to make a reading at the first minute after ignition), until the highest temperature is reached, a point which must be carefully noted. The temperature will now begin to fall slowly, and readings at intervals of a minute must again be made for about ten minutes. During the experiment the outer vessel should be stirred occasionally and its temperature taken.

This completes the series of observations. The bomb is removed from the calorimeter and carefully dried. The needle valve *B* is slowly opened so as to allow the gases to escape from the bomb. When the pressure has fallen again to that of the atmosphere the cover is removed and the interior of the bomb cleaned and dried. Any of the iron wire which has not been oxidized should be

detached and weighed, and the weight subtracted from that originally taken.

Calculations. For approximate work the "heat-loss correction" can be made by the simple graphical method previously described (p. 189), but this is not accurate when the passage of heat is slow, and one or other of the various improved correction methods[2] should be used, such as the "3-period method" described below.

"*Heat-loss*" *correction.* For the purpose of this correction one can assume that the heat exchange between calorimeter and surroundings is due to two factors—(a) conduction, convection and radiation to the outer vessel, and (b), Joule heating by the working of the stirrer. The rate of rise of temperature due to (a) is approximately proportional to
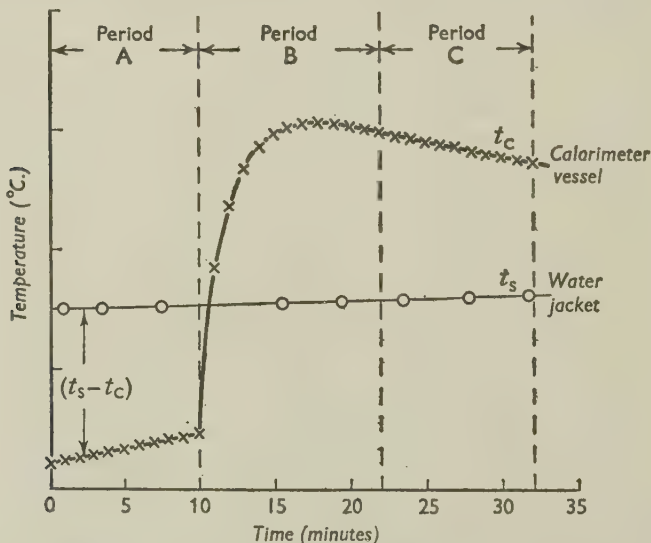
FIG. 9.4. Temperature record for heat-exchange correction by the 3-period method.

(temperature of the outer jacket—temperature of the calorimeter), according to Newton's Law of Cooling, while the rate of rise due to the stirrer is constant. Thus, the rate of gain of heat should be represented by the equation, $dQ/dt = k_1(t_s - t_c) + k_2$, where dQ is the heat in calories gained in time dt when the temperature of the calorimeter is t_c and that of the surrounding jacket is t_s. To apply this theory one must, in effect, determine the constants k_1 and k_2, and this can be done from the temperature-time data.

First, complete temperature–time graphs for the calorimeter (t_c) and the water-jacket (t_s) must be plotted; clearly, t_c and t_s must be in the same units, and therefore the Beckmann readings should be converted to °C by making use of the preliminary comparison readings which have been

made for this purpose (p. 195). Fig. 9.4 shows the kind of graphs which should be obtained. The chart can clearly be divided into three distinct periods, namely, a preliminary rating period (A) during which t_c is rising slowly and regularly, the combustion period (B) during which heat is being transmitted from the bomb to the calorimeter, and a final rating period (C) during which t_c falls regularly. The temperature of the outer jacket, t_s, may perhaps rise slightly during the course of the experiment, as indicated in Fig. 9.4.

The above heat exchange equation can now be tested for periods A and C. The rate of change of temperature (per minute) is obtained by sub-tracting consecutive readings of t_c, and the difference between the tempera-ture of the calorimeter and its surroundings can be measured on the graph for the time half-way between the two temperature readings. A graph of δt_c against $(t_s - t_c)$ can then be plotted. The data shown in Fig. 9.4 would lead to a "heat correction graph" like that shown in Fig. 9.5, a number of points being obtained from period A with positive values of $(t_s - t_c)$ and of δt_c, and other points from period C, during which $(t_s - t_c)$ is negative. Between the two sets of points no data are available, but, if the above equation is correct, the δt_c against $(t_s - t_c)$ graph should be a straight line; con-sequently, linear interpola-tion is permissible. (If the stirrer produces appreciable heating effect, a positive value of δt_c will be found for $(t_s - t_c) = 0$).

The "heat-loss" graph can now be used to calculate the heat loss or gain which the calorimeter must have ex-perienced during the period

Fig. 9.5. Calculation of heat-exchange correction (see text).

B. For each minute one calculates the mean calorimeter temperature t_c, and then the difference $(t_s - t_c)$—paying due regard to sign. The heat *gain* δt_c is then read from the correction graph; values will be positive while $t_s > t_c$, and then become negative when $t_s < t_c$. Positive values of δt_c mean that the calorimeter has been gaining heat from the surroundings, equal to $\delta t_c \times W$ (where W is the total water-equivalent) during that minute; negative values show that heat loss must have been occurring. Since W is a constant, $W\Sigma\delta t_c$, taken over period B, gives the total number of calories which the calorimeter has *gained* from the outside during period B. If the overall change of temperature from the beginning to the end of period B is $T°$, the corrected rise due to the heat of combustion alone is $(T - \Sigma\delta t_c)$. Of course, if on the whole there has been a loss of heat (as, for example, is true for the hypothetical experiment illustrated in Fig. 9.4), one would find $\Sigma\delta t_c$ negative, and therefore the corrected rise of tempera-ture would come out greater than the observed—as it must.

As a check on the calculation, one should calculate the corrected temperature rise for several points subsequent to the maximum in the curve; a constant corrected value should be found for the heat due to the combustion.

Water-equivalent of the calorimeter.   As explained above, it is necessary to make preliminary determinations with benzoic acid in order to find the water-equivalent of the calorimeter.   Since the amount of water used in different experiments may, perhaps, be varied, it is usual to calculate the water-equivalent of the bomb and calorimeter vessel separately.   Allowance should be made for the small amount of heat produced by combustion of the iron wire (if used), the heat of combustion of iron being 1·6 kcal/g.   It follows that the heat balance for the calibration experiment gives

$$\begin{pmatrix} \text{wt. of} \\ \text{benzoic} \\ \text{acid} \end{pmatrix} \times 6{,}318 + \begin{pmatrix} \text{wt. of} \\ \text{iron} \\ \text{burnt} \end{pmatrix} \times 1{,}600 = \begin{pmatrix} \text{corrected} \\ \text{rise of} \\ \text{temperature} \end{pmatrix} \begin{pmatrix} \text{wt. of} \\ \text{water} \end{pmatrix} + \begin{pmatrix} \text{water-equivalent} \\ \text{of calorimeter} \end{pmatrix}$$

Two or more calibration experiments should be carried out until concordant values are obtained for the water-equivalent of the calorimeter.

Heats of combustion.   When the apparatus has been calibrated, as described above, exactly similar determinations are made with the substance for which the heat of combustion is required (e.g. sucrose, anthracene, coals, etc.).   Volatile liquids can be burned by enclosing them in a gelatine capsule of known weight and calorific value.

The method of calculating the heat of combustion from the corrected temperature rise will be apparent.

Bomb calorimetry is applicable to a wide variety of substances, but complications arise for substances containing sulphur, nitrogen, phosphorus, etc., since one must know the products formed in the reaction.

BIBLIOGRAPHY 9B: The bomb calorimeter

Weissberger, Vol. 1, Pt. 1, Ch. 14.

[1] Jessop, *J. Res. Nat. Bur. Standards*, 1942, **29**, 247.

[2] See, for example, White, *The Modern Calorimeter*, 1928 (Chem. Cat. Co., New York); Coops and van Nes, *Rec. trav. chim.*, 1947, **66**, 161.

THE CONDUCTIVITY OF ELECTROLYTES

10A. THEORY AND TECHNIQUE

Terminology. An electric current may be carried either by electrons —as in metals and most "semi-conductors"—or by movement of ions; conduction in *liquid* solutions is entirely *electrolytic.* The conduction obeys Ohm's Law, i.e. the current (in amperes) = difference of potential (volts)/resistance (ohms). The resistance between opposite faces of a unit cube of a conductor is called the *specific resistance* or *resistivity.* The reciprocal of resistance is *conductance,* and the reciprocal of specific resistance is *specific conductance* or *conductivity* (symbol κ; units ohm^{-1}cm^{-1} or "mhos").

With electrolytic solutions conductance is a more natural quantity to employ than resistance, since it is related directly to the number of ions present and to their rate of movement. Generally the pure solvent is practically non-conducting, and consequently the observed conductance is due entirely to dissolved electrolyte. In comparing the conducting properties of different substances one should compare chemically comparable quantities of the substances, e.g. equivalent or equi-molar quantities. If the concentration of the solution is c g equivalents per litre, the specific conductance (κ) is clearly due to $c/1,000$ g equivalents, and the theoretical conductance for 1 g equivalent would be $\kappa \times 1,000/c = \Lambda$, the *equivalent conductivity.* The *molar conductivity* is similarly $\kappa \times 1,000/m$, where m is the molarity of the solution.

Theory. The equivalent conductivity, Λ, of a solution is a measure of the number and rate of migration of anions and cations from 1 g equivalent of the solute. Experiment shows that Λ increases as the solution is diluted (whereas κ, of course, decreases). The increase of Λ with dilution could arise from either an increase in the number of ions present (i.e. increased dissociation) or from a greater speed of movement of the individual ions. Arrhenius (1883) put forward the former explanation and assumed that the true ionic mobilities were independent of concentration so that Λ is proportional to the number of ions present. According to the law of mass action all dissociation processes should tend to completion as the concentration tends to zero, and hence the equivalent conductivity at zero concentration Λ_0 represents the current-carrying capacity of the solute in

a completely dissociated state.   The conductivity at finite concentrations, Λ_c, should therefore give the degree of dissociation, α, from $\alpha = \Lambda_c/\Lambda_0$.   The Arrhenius theory is approximately correct for *weak electrolytes*, i.e. solutes which are only slightly ionized, and for such substances conductivity measurements can be used to obtain the degree of dissociation and hence the mass action dissociation constant (p. 211).

Salts of strong acids and bases also show Λ increasing with dilution, but this cannot be ascribed to increasing ionization as salts are known to be ionized even in the solid state.   The effect is due to interaction between the anions and cations, tending to retard their movements.   In extreme cases, particularly with polyvalent ions, temporary "ion-pairs" may form owing to the strong coulombic forces, but otherwise the interaction is a statistical "ionic atmosphere" effect.   The theory was developed by Debye and Hückel (1923) and Onsager (1926, 1927), who obtained an expression for the conductivity of very dilute solutions which is of the form

$$\Lambda_c = \Lambda_0 - (a\Lambda_0 + b)\sqrt{C}$$

where C is the concentration, and a and b are constants which can be evaluated from the theory.   (For a uni-univalent electrolyte at 25° C, $a = 0.2273$, and $b = 59.78$.)   In practice, graphs of Λ_c against $\sqrt{C}$ are approximately linear, and do approach the correct slope of the Onsager theory at great dilutions ($C \to 0$).   Appreciable departures from the theory occur, however, at quite moderate concentrations, and Λ_0 cannot be obtained accurately by graphical extrapolation of data.   Instead, it is better to assume the constants of the Onsager equation and calculate Λ_0 from the equation in the form

$$\Lambda_0 = \frac{\Lambda_c + b\sqrt{C}}{1 - a\sqrt{C}}$$

At the present time there is no quantitative theory for the conductance of concentrated solutions of strong electrolytes.

Outline of experimental methods.   Resistance is almost always measured by means of a Wheatstone bridge circuit (Fig. 10.1). S is a source of e.m.f.; C is the unknown resistance; R_1, R_2 and R_3 are standard resistances, and D is a detector. R_3 is adjusted until the detector indicates no e.m.f. between the points 2 and 4.   The bridge is then said to be "balanced," and the resistances must be related by the expression $R_1/R_2 = R_3/C$ so that $C = R_2R_3/R_1$.

With an electrolytic conductor there are several complications that do not arise with electronic conductors.   The principal one is that the passage of a current causes electrolysis, and a back e.m.f. of "polarization" is set up.   This difficulty is overcome by using an

alternating current so that whatever electrolysis occurs during the first half-cycle is reversed during the second, and the net electrolysis is negligible.   Now it becomes necessary to use for D in place of the

usual moving coil galvanometer an instrument capable of detecting small a.c. voltages of the order of 1 millivolt or less.   The oldest and still most satisfactory technique for laboratory work is to apply an audio-frequency signal to the bridge and detect the point of balance by disappearance of the sound in sensitive earphones.   A further complication is that, whereas a d.c. Wheatstone bridge is purely resistive, an a.c. circuit responds to inductance and capacity as well as resistance, and a perfect

Fig. 10.1.   Basic Wheatstone bridge circuit for measurement of resistance.

null cannot be obtained unless the bridge is balanced for resistance and reactance.   Consequently, the standard resistors must be non-inductively wound, and it is generally necessary to introduce a variable condenser in parallel with one arm of the bridge to balance out stray capacity.   Also, for work of high accuracy, the correct earthing of the bridge is important because of asymmetric capacity to earth.   In spite of these complications conductivity has been

Fig. 10.2.   Kohlrausch's conductivity apparatus.

measured with a relative accuracy as high as 1 part in 10^6.

Kohlrausch's apparatus.   The classical early work of Kohlrausch (1898) and others was done with the simple circuit shown in Fig. 10.2.   The source of sound is a small induction coil ("buzzer"), I, producing a note of high pitch; R is a resistance box, and the bridge is adjusted by moving the contact x on a straight slide-wire axb until the sound in the earphones is at a minimum.   The

sharpness of the minimum can generally be improved by connecting a variable air condenser in parallel with R, and adjusting it also to minimum sound.   A quiet laboratory is needed, and direct sound from the buzzer can be largely eliminated by placing the latter in a

box filled with cotton-wool. At the balance point $C = R \times xb/xa$.
An accuracy of about 1% is readily obtainable with this simple
form of apparatus. Some of the later improvements in technique
are described below.

Signal generator. The signal produced by an induction coil is far
from being of ideal sine-wave form, and the frequency and intensity
are not easily controllable. Nowadays valve oscillators are generally
employed for conductivity work. A high-frequency source would be
desirable to reduce polarization but increase of frequency increases
stray reactance; in practice a frequency of 1,000 to 3,000 cycles per
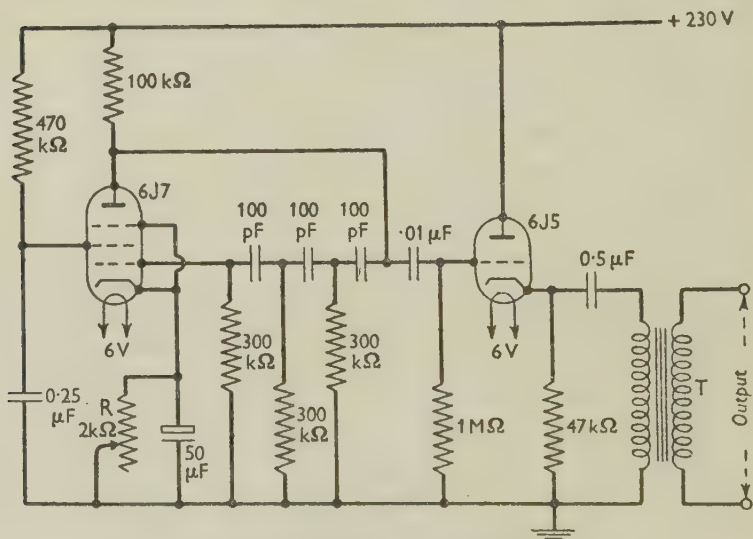
FIG. 10.3. Valve oscillator circuit for conductivity bridge.

second (to which the ear is most sensitive) is chosen as a com-
promise.

Many valve oscillator circuits have been described.[1] That shown
in Fig. 10.3 is easily constructed from standard radio components
and gives a signal of good wave form and of ample intensity which
can be adjusted by the variable resistance R. (The circuit shown is
for operation from the 230 V mains, but it can, of course, be readily
modified for use with battery valves, if desired. Oscillators of
various degrees of elaboration are available commercially.) The
signal (which should be about 1 volt) is fed to the bridge by a low-
ratio transformer (T) in order to isolate the bridge from the h.t.
of the oscillator circuit. The oscillator should be placed at least
10 ft from the bridge and the leads should be of the screened type.

The bridge. The "ratio arms" of the bridge (R_1 and R_2 in Fig. 10.1) should be accurate non-inductive fixed resistors. Shedlovsky[2] recommends making $R_1 = R_2 = 1,000\ \Omega$; then R_3, when adjusted for balance, reads directly the resistance of C. An adjustable ratio box is sometimes used, by means of which R_1/R_2 can be made 100/1,000, 1,000/1,000, 1,000/100, etc., so that the bridge can cover a wider range of resistance.

The variable resistance R_3 should be a decade box of low-inductive resistors such as that shown in Fig. 10.4. If equal ratio arms are used, the decade box should cover the range from 1 to 100,000 Ω, but 1 to 10,000 Ω will suffice for most purposes if 10 : 1 and 1 : 1 ratio arms are to be employed. For the highest accuracy Shedlovsky[2] suggests that all the bridge resistances should be kept within the range
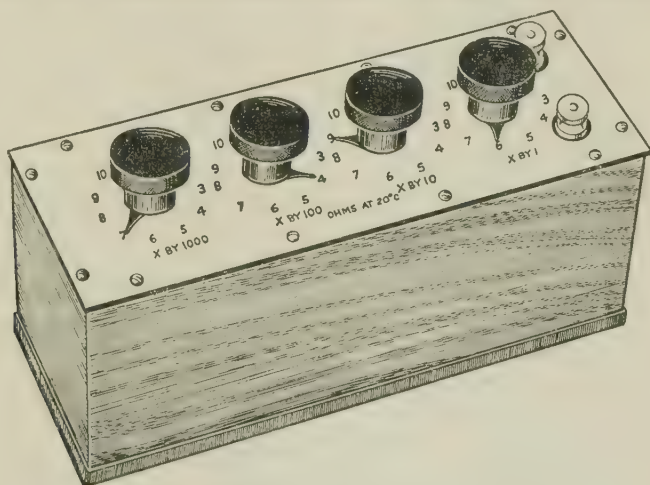
Fig. 10.4. Decade box of low-inductive standard resistors.
(Courtesy Messrs. H. Tinsley and Co., Ltd., London.)

1,000–10,000 Ω, and, if cell resistances above 10,000 Ω have to be measured, the cell should then be shunted by a calibrated 10,000 Ω resistor in parallel and the cell resistance calculated from the measured resistance by the law of parallel resistances. All connections in the bridge should be made with straight, stiff wires well separated.

Bridge balance detector. A sensitive pair of earphones of fairly high resistance should be used to detect the point of balance. If the apparatus is used in a quiet laboratory it may be found possible to find the balance without applying any amplification, but it is normally necessary to interpose a valve amplifier between the bridge and the earphones to make it easier to differentiate clearly between

small signals near the balance point.   This practice is much better than applying a higher voltage to the bridge as that increases the liability to polarization and heating.

Fig. 10.5 shows the circuit of a satisfactory 2-valve mains-operated amplifier which can be constructed readily from standard radio components, but naturally, any other amplifier could be used, as the requirements are not critical.   A battery-operated circuit offers the advantages of simplicity and complete freedom from "mains hum". The out-of-balance signal from the bridge is preferably fed to the amplifier by a low-ratio audio-frequency transformer.

Several valve circuits providing *visual* indication of bridge balance
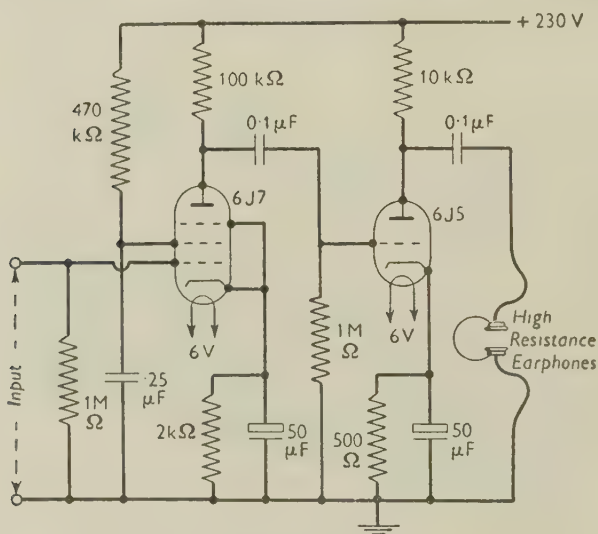
Fig. 10.5. Simple bridge amplifier circuit.

have been described.[3]   The use of the "magic eye" detector is convenient for routine measurements.[3]

Capacity balance.   It has been mentioned that a perfect balance on an a.c. bridge cannot be expected unless reactance is balanced as well as resistance, and this condition is usually achieved by adding a variable condenser to one arm of the bridge and adjusting it to give the sharpest minimum of sound.   A convenient arrangement is to use a *differential* variable air condenser, Z, of capacity about 100 $\mu\mu$F, the fixed sides being connected to points 1 and 3 (Fig. 10.6) and the movable vanes being connected to point 4.   Capacity can then be applied in parallel with either R_3 or C as required by simply turning the insulated knob of the condenser.   The procedure is to

balance the bridge first by adjusting R_3 as well as possible, then
adjust the condenser for minimum sound, and finally readjust R_3.

Earthing. The following points in the circuit should be connected
to earth: the chassis of the oscillator and amplifier, all screens sur-
rounding leads or resistance boxes, the thermostat, and the point 4
on the bridge. (Fig. 10.6.) This earthing arrangement should be
found quite satisfactory if measurements are to be made of resist-
ances ranging from about 100 to 10,000 Ω with a sensitivity of 0·1%.
For work of higher precision it is essential that the Wagner earthing
circuit be employed; reference should be made to original papers for
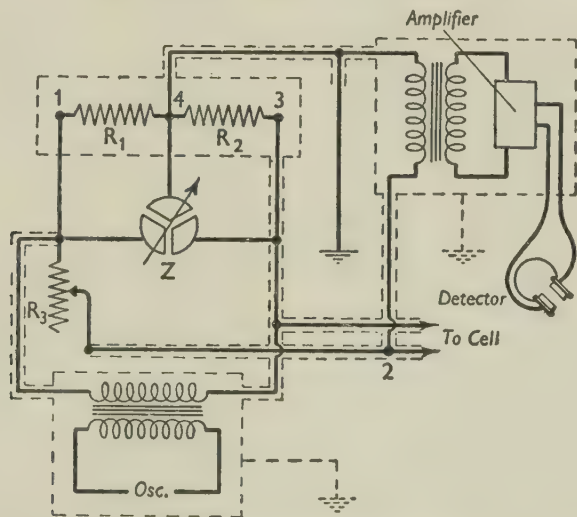
FIG. 10.6. Earthing of components in the conductivity bridge.

this and other refinements used in the most accurate research
work.[4]

Temperature control. As the conductivity of solutions varies by
about 2 per cent per degree, the temperature must be controlled to
within 0·05–0·01° C if an accuracy of 0·1% is to be obtained on κ.
Consequently, the conductivity cell must be immersed in an efficient
thermostat bath. Oil thermostats are preferred for research work
on conductivity because electrical leakage is thereby minimized, but
an ordinary water thermostat is more convenient. A simple method
of supporting the cell in the thermostat is to place it in a small "box"
made of copper sheet which can be hung on the side of the tank.
The "box" is partially open at the ends so that water from the
thermostat can pass through it.

Conductivity cells.   Fig. 10.7 shows a number of conductivity cells for various purposes: (a) and (b) are suitable for accurate measurements, (a) for solutions of high conductance, and (b) for those of
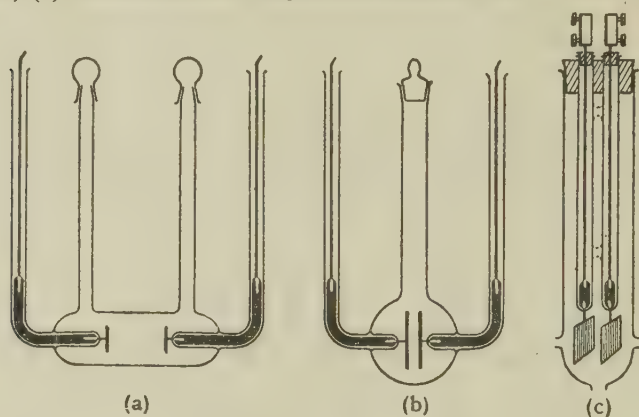
FIG. 10.7. Conductivity cells.
(a) For liquids of high conductance.
(b) For liquids of low conductance.
(c) Dipping cell.

low conductance; (c) is a simple dipping cell, which is convenient for approximate work and conductimetric titrations.   The cells should be made of Pyrex or other resistance glass, and the electrodes of platinum sufficiently thick to be quite rigid.   Connection to the electrodes is made by a drop of mercury, but it is convenient to seal the ends of the tubes with wax and attach brass connectors (as in Fig. 10.7 (c)) so that the cells can be inverted during washing, etc.

All glass vessels in conductivity work should be very thoroughly washed free from electrolyte.   After the usual cleansing with chromic acid and repeated rinsing with distilled water, they should be steamed out by being inverted over the tube T of the flask shown in Fig. 10.8.   Water is boiled in the flask, steam passes up through the tube and the condensate collects in the funnel.   Finally, the vessel may be dried by drawing a current of air through it while it is still warm.
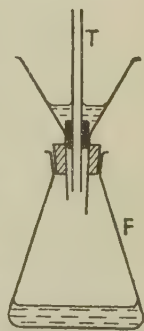
FIG. 10.8. Flask for steaming glass vessels.

Platinizing the electrodes.   Even with a.c. current some polarization occurs if *smooth* platinum electrodes are used, but it can be eliminated by coating the electrodes with a thin layer of platinum black.   This has the effect of increasing the effective area for current

discharge, thus reducing the local current density, and it also catalyzes the electrode processes.

The electrodes are platinized by electro-deposition from a solution consisting of 2 g platinic chloride and 0·02 g lead acetate in 100 ml of water. The current from 2 accumulators is regulated by a rheostat so that only a moderate stream of gas is formed at the electrodes. The current is reversed every half-minute, and after about 10 minutes the electrodes should be sufficiently coated. For work with dilute solutions only a very thin coating should be applied.

After the electrolysis, great care must be taken to remove all traces of the platinizing solution, which is liable to be adsorbed by the electrodes. It is advisable to replace the platinizing solution by a dilute solution of sulphuric acid and pass a current for some time in each direction. This treatment should be followed by repeated rinsing with warm distilled water and then with conductivity water (see below). Cells should be kept filled with pure water when not in use.

Conductivity water. Ordinary laboratory distilled water generally has a conductivity of about $3-5 \times 10^{-6}$ mho. Most of this conductivity is due to impurities, and very little to ionization of the water itself, as the value has been reduced

FIG. 10.9. Simple still for producing small quantities of conductivity water of $\kappa \gg 10^{-6}$ mho.

to $0·04 \times 10^{-6}$ mho by extreme purification. Dissolved carbon dioxide in equilibrium with that in the air produces a conductivity of about $0·8 \times 10^{-6}$ mho and the remainder is due to traces of salts, ammonia, etc. Elaborate precautions are required in order to produce water of conductivity less than $0·1 \times 10^{-6}$ mho; the principle usually employed is to redistil good distilled water with the addition of alkaline permanganate and to condense and reject part of the steam, the remainder being condensed in a tube of pure tin or silica in a stream of purified air.[5]

The apparatus shown in Fig. 10.9 is suitable for preparing small

quantities of conductivity water of sufficient purity for most pur-
poses ($\kappa \not> 1 \times 10^{-6}$ mho).   Distilled water to which a little sodium
hydroxide and potassium permanganate have been added is boiled
in a large copper steam-can, A, over a gas ring.   The steam passes up
a Pyrex glass column, B, which is loosely packed with short pieces of
Pyrex tubing.   This column acts as a spray trap and also condenses
part of the steam, thus keeping the column washed by "counter-
current" flow.   The remainder of the steam is condensed in the
Liebig condenser D (Pyrex) and collected in the Pyrex flask E.   The
stopcock F is placed at the bottom of the flask so that the
stock of water can be removed completely. G is a small soda-lime
tube to prevent entry of CO_2. D and E may at first give out traces
of alkali from the glass, but this is gradually removed by "ageing".

The still is run for some time, the first distillate being rejected
until its conductivity has fallen below 1×10^{-6} mho; a stock of
conductivity water is then collected and drawn straight from the
flask for making up solutions.

Preparation of conductivity water by means of ion-exchange resins.
The simplest method of obtaining water of low conductivity is by
passing it slowly through a column packed with a mixture of
anion- and cation-exchange resins, the former being in the —OH
form and the latter in the —H form.   Such a mixture is supplied
by the Permutit Co., Ltd., London, under the name "Bio-Demin-
rolit".   Anions present in the water are replaced by OH^- ions,
and cations by H^+ ions, and since these are in equivalent pro-
portions, the water is "de-ionized" completely.   After two or
three "bed-volumes" of water have been passed through the column,
the specific conductivity of the effluent falls to about $0 \cdot 1 \times 10^{-6}$ mho,
or less.   If the column is fed with ordinary distilled water, it will
treat a very large volume of water before it requires regenerating.
When necessary, this is effected by first separating the two types of
resin (by an upward flow of water) and then treating the anion-
exchanger with excess of NaOH in a column and the cation-
exchanger with excess of HCl.   The two resins are then washed
and mixed again for use.

Preparation of solutions.   Since much of the theory of conductivity
is concerned with very dilute solutions and since their conductivity
can be measured with considerable accuracy, it is necessary to make
sure that the concentration of the solutions studied is known with
similar accuracy.   The usual procedure is to prepare first the most
concentrated solution required and to dilute it successively.   Dilu-
tion by volume is hardly accurate enough, and therefore the solutions
should be made up and diluted *by weight*.

A number of wide-necked stoppered Pyrex flasks of about 150 ml

capacity are cleaned, steamed out, and dried as described above. A suitable quantity of the substance is weighed accurately from a weighing bottle into one of them. The flask is then weighed to the nearest centigram on a large balance, conductivity water is added, and the flask weighed again. More dilute solutions are subsequently prepared from this solution by pouring some of it into another (weighed) flask, adding conductivity water, and weighing again. Buoyancy corrections should be applied where significant (pp. 26–7).

Determination of the cell constant. The cells used for conductivity measurements are not of accurately known dimensions, and consequently they need to be calibrated before it is possible to deduce values of specific conductance from measurements of cell resistance. This is done by means of solutions of accurately known conductivity. Suppose a given cell, when filled with a solution of known specific conductivity κ is found to have a resistance R, then the *cell constant*, K, is defined by $K = \kappa R$. The cell constant may therefore be thought of as the resistance that the cell would exhibit when filled with liquid of unit conductivity. If another solution shows a resistance R' when measured in the same cell, its conductivity κ' is obtained from the same equation, i.e. $\kappa' = K/R'$.

Conductivity cells are generally calibrated with solutions of potassium chloride of carefully adjusted concentration and at a temperature of $25 \cdot 00°$ C. In the following table [6] are given the values, in reciprocal ohms, of the conductivity of solutions containing 0·1 and 0·01 gram-equivalent (1 g equiv. $= 74 \cdot 553$ g) of potassium chloride in one *cubic decimetre* (0·999973 litre). These solutions can be prepared from 7·4789 and 0·74625 g of KCl in 1,000 g of water, all weights having been corrected for the buoyancy of the air (pp. 26–7). (The concentration of 1 g equiv. per 1,000 g *of solution* is called "demal"; it differs slightly from a *normal* solution.)

Temperature	Conductivity ohm⁻¹ cm⁻¹	
	0·1 demal	0·01 demal
0°	0·007138	0·0007736
18°	0·011167	0·0012205
25°	0·012856	0·0014088

A quantity of pure, dry KCl is weighed out, and the necessary quantity of water to produce exactly 0·1 or 0·01 demal is calculated and then obtained by adjustment (using a robust balance). Alternatively, if an accuracy of 1 part in 1,000 is sufficient, the solution may be made by dissolving any weighed quantity of KCl in a graduated flask of water and, after bringing the temperature to $25°$ C, making

up by volume to the mark.   The concentration of the solution is then known in terms of g equiv. per litre, and the conductivity can be calculated from an empirical equation given by Shedlovsky [7] for KCl solutions at 25° C, namely:

$$\Lambda = 149 \cdot 82 - 93 \cdot 85\sqrt{C} + 94 \cdot 9C(1 - 0 \cdot 2274\sqrt{C})$$

where C is the concentration in g equiv. per litre.

Another procedure is to make up a solution by weight (without, however, adjusting the quantities) and then use Shedlovsky's formula together with the density, which for KCl solutions up to $0 \cdot 1N$ is given by $\rho_c = 0 \cdot 9971 + 0 \cdot 047C$.

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10B.   WEAK ELECTROLYTES

EXPERIMENT

Determine the equivalent conductivity of a weak acid at several concentrations and hence calculate the dissociation constant of the acid.

Suitable acids for this experiment are succinic, benzoic, and mandelic acids.   Weak dibasic acids such as succinic behave in conductance measurements as monobasic acids since only the first hydrogen is ionized at the concentrations employed.

Procedure. If an accuracy of better than 1% is required, the solutions must be made up by weight rather than volumetrically. The acid should be weighed out into a steamed Pyrex flask fitted with a stopper, and a quantity of conductivity water sufficient to make a solution of about $N/20$ should be added and weighed.   More dilute solutions are then prepared from the stock solution by repeated dilution by weight in other Pyrex flasks, the concentration being approximately halved each time.   The flasks are suspended in the thermostat at $25 \cdot 00°$ C in readiness for the measurements of the conductivity of the solutions.

For weak electrolytes a cell having a small cell constant should be used. To make a determination, the cell is rinsed with a little of the solution and then filled and placed in the thermostat. The leads are connected and the balance point of the bridge is determined. The cell is left in the thermostat until the resistance becomes constant, showing that the solution has come to $25 \cdot 00°$ C. The cell is then emptied, and the measurements are repeated with a further sample of the same solution as a check. This check is particularly necessary with very dilute solutions where appreciable amounts of substance derived from a previous solution may be slowly desorbed from the electrodes. When concordant results have been obtained with the first (most concentrated) solution, the cell is washed with water and then rinsed twice with the next solution, the conductivity of which is then determined in the same way. A series of solutions of increasing dilution down to about $N/1,000$ is studied, and the conductance of the water alone is also obtained. The constant of the cell used must, of course, be determined with a standard KCl solution as described, but a rather dilute solution is necessary if the resistance of the cell is not to be too low for accurate measurement. (Alternatively, the conductance of the most concentrated acid solution employed may be measured both in a cell of small constant and also in one of larger constant, and the absolute cell constant of the latter may be determined with one of the standard KCl solutions referred to on p. 209. Hence the cell constant of the first cell can be calculated.)

Treatment of results (elementary theory). The molar concentration of each solution is calculated, and then its specific conductance and hence equivalent conductivity. If the conductivity of the water is less than 1×10^{-6} mho it may be ignored, but if larger, it should be subtracted from that of the solutions before calculating Λ. In order to calculate the degree of dissociation one needs Λ^0, but, in the case of weak electrolytes, this cannot be obtained reliably by extrapolation, and it is therefore calculated from the sum of the ionic conductivities. The following values may be taken for Λ_0 at $25°$ C: acetic acid $390 \cdot 8$, benzoic acid 383, mandelic acid 378, succinic acid 382. The degree of dissociation is calculated for each solution as $\alpha = \Lambda_c/\Lambda_0$. The values of α are then substituted in the Ostwald Dilution Law to give the dissociation constant, $K = \alpha^2/(1-\alpha)V$, where V is the volume in litres containing 1 mole of acid. The resulting values of K should be approximately constant over a considerable range of concentration.

Improved treatment for weak electrolytes. There are two distinct reasons why the elementary theory does not give absolutely constant values for the dissociation constant.

(a) The degree of dissociation is not accurately given by $\alpha = \Lambda_c/\Lambda_0$ because the ionic mobilities change with ionic concentration. A correction can be applied as follows, using the method of successive approximations. First the "classical" value of α is obtained as above. This is then

substituted in the Onsager equation to calculate the value of Λ (say Λ') which the ions would exhibit at the actual ionic concentration present in the solution (i.e. at αC). Thus,

$$\Lambda' = \Lambda_0 - \sqrt{\alpha C}(a\Lambda_0 + b)$$

$$= \Lambda_0 - \sqrt{(\Lambda_c/\Lambda_0)C}(0 \cdot 2273\Lambda_0 + 59 \cdot 78)$$

The new value, Λ' is now used in place of Λ_0 to calculate an improved value of α, say, $\alpha' = \Lambda_c/\Lambda'$. A second value of Λ (say Λ'') may be calculated in the same way, giving a further refinement of α (α'') and so on. Usually two recalculations give a substantially constant value of α, which may then be used to calculate $K(= \alpha''^2/(1-\alpha'')V)$.

(b) In calculating K one ought to use activities rather than concentrations. For very weak acids little error will be introduced since the ionic strength is very low, and the ions and the undissociated acid will have activity coefficients very close to unity. For moderately weak acids, however, a correction becomes necessary for the ionic species—say if the ionic strength exceeds $10^{-4}N$. Thus, if C_i is the concentration of hydrogen ions (and of anions) and C_u is concentration of undissociated acid, the thermodynamic dissociation constant is given by $K_{Th} = (C_i \cdot f_\pm)^2/C_u$, where $f_\pm$ is the mean ion activity coefficient. Such activity coefficients are known to follow the law $\log f_\pm = -A\sqrt{C_i}$, where A is a constant (about $0 \cdot 5$, according to the Debye-Hückel theory). Hence,

$$\log K_{Th} = \log (C_i^2/C_u) - 2A\sqrt{C_i} = \log K_c - 2A\sqrt{C_i}$$

where K_c is the concentration mass-action constant calculated as explained under (a). Thus, a graph of $\log K_c$ against $\sqrt{C_i}$ should give a straight line from which $\log K_{Th}$ can be obtained as the intercept at $C = 0$, and the slope gives $2A$.

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10C. STRONG ELECTROLYTES

EXPERIMENT

Determine the equivalent conductivity of solutions of a strong electrolyte, and hence examine the validity of the Onsager theory as a limiting law at great dilutions.

Suitable electrolytes are HCl, KNO_3, $AgNO_3$, NaCl. (Unidivalent salts may also be studied, but di-divalent salts such as $CuSO_4$ and $MgSO_4$ are only partially dissociated on account of ion-pair formation.[1]

Procedure. The solutions are prepared and their conductivity measured in the manner described above for weak acids. Concentrations from about $N/10$ to about $N/10,000$ should be studied. This necessitates the use of two cells of high and low cell constants

to cover the whole range accurately. The conductivities should be corrected for that of the water.

Treatment of results. Since the Onsager equation gives $\Lambda_c = \Lambda_0 - (a\Lambda_0 + b)\sqrt{C}$, a graph should be plotted of Λ_c against $\sqrt{C}$. This should tend to linearity as $C \to 0$. The limiting straight line should be drawn and its slope determined and compared with that given by the Onsager theory, namely, $-(a\Lambda_0 + b)$ where $a = 0.2273$ and $b = 59.78$ for a uni-univalent electrolyte at $25°$ C. Λ_0 is obtained by extrapolation of the limiting line to $C = 0$. If the limiting slope is in reasonable agreement with the Onsager equation, the theory may be assumed correct and a more reliable value of Λ_0 may be calculated from the experimental values of Λ_c for the most dilute solutions by means of the expression $\Lambda_0 = (\Lambda_c + b\sqrt{C})/(1 - a\sqrt{C})$ (i.e. a theoretical extrapolation rather than a graphical one).

Shedlovsky[2] showed that conductivity data for strong electrolytes can be represented within an accuracy of 0.1% up to concentrations of $0.1N$ by an *empirical* extension formula from the Onsager equation, namely, $\Lambda_0 = [(\Lambda_c + b\sqrt{C})/(1 - a\sqrt{C})] - AC$, where A is a constant to be determined empirically. Such formulae are useful for interpolation and for representing data in a concise form. (See the case of KCl solutions, mentioned on p. 210.)

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10D. APPLICATIONS OF CONDUCTANCE MEASUREMENTS

Since the measurement of electrical conductance of solutions can be made accurately and conveniently, it provides a valuable means of studying many problems in physical chemistry, as may be seen from the following examples. The use of conductance to determine the concentration of a solution of a pure substance by comparison with previously prepared calibration curves is sufficiently obvious to need no further exemplification. The method can frequently be used to advantage when the substances to be determined are not readily estimated by simple analytical methods.

Solubility of sparingly soluble salts. The conductance method is applicable for finding the concentration of the saturated solution, provided that the salt is not hydrolyzed, and that the solubility is not too high. It may then be assumed that the ions possess their limiting conductivities, and Λ_0 may be taken as the sum of the ionic conductivities: these must, of course, be known for the same temperature. Hence, measurement of the specific conductivity of the saturated solution leads to a value for the concentration. A refinement of the calculation is to correct Λ_0 by use of the Onsager equation to allow for the finite concentration.

EXPERIMENT

Determine the solubility of lead sulphate, or of silver chromate, in water at 20° C.

Procedure. The conductivity of the water employed should first be determined at 20°. A quantity of finely powdered lead sulphate or silver chromate is then shaken repeatedly with the conductivity water in order to remove any impurities of a comparatively soluble nature. The well-washed salt is then placed with conductivity water in a hard-glass vessel, which is placed in a thermostat at 20°, and shaken from time to time. After intervals of about quarter of an hour, a quantity of the solution is transferred to a conductivity cell, and the conductivity determined. A conductivity cell with large electrodes placed a short distance apart should be used. This is repeated with fresh samples of the solution, until constant values are obtained.

The conductivity so determined is corrected by subtracting the conductivity of the water employed, and the solubility then calculated by means of the equation $c = 1,000 . \kappa/\Lambda_0$. This gives the number of gram-equivalents of salt in 1 litre of solution (or of water). To obtain the number of gram-molecules per litre, the solubility in gram-equivalents per litre must be divided by the valency of the metal. (For the solubilities of some sparingly soluble salts, see Appendix, Table A9.)

Hydrolysis of salts. When the salt of a weak acid or base is dissolved in water, hydrolysis occurs, so that the conductance of the solution is now due partly to the ions of the salt and partly to the ions of the acid or base formed by hydrolysis (more especially the hydrogen ion and hydroxide ion). If, however, a quantity of the weak acid or base which, in the presence of its salt, can be regarded as completely un-ionized, is added to the solution, the hydrolysis of the salt will be diminished, but the ionization will be unaffected. From measurements of the conductivity of pure solutions of the salt (in which, therefore, hydrolysis occurs), and of solutions containing excess of the weak base or acid, the degree of hydrolysis can readily be calculated.

Considering here only the simplest case of a binary salt, say of a strong monobasic acid with a weak monoacid base, the hydrolytic equilibrium is given by the expression

$$\frac{K_b}{K_w} = \frac{(1-\alpha)V}{\alpha^2}$$

where V is the volume in litres containing 1 gram-molecule of salt; α the degree of hydrolysis; K_b the affinity constant of the weak base; and K_w the ionic product of water. The amount of the unhydrolyzed salt is represented by $(1-\alpha)$, and of the free acid by α. The equiva-

lent conductivity, Λ_v, of the solution of hydrolyzed salt, therefore, is given by

$$\Lambda_v = (1-\alpha)\Lambda_v' + \alpha\Lambda_v''$$

where Λ_v' and Λ_v'' are the equivalent conductivities at the dilution V litres of the unhydrolyzed salt and of the strong acid respectively. The former, as has been pointed out, can be determined by measuring the equivalent conductivity of the salt in presence of excess of the weak base.   The degree of hydrolysis of the salt at the given dilution is then given by the expression

$$\alpha = \frac{\Lambda_v - \Lambda_v'}{\Lambda_v'' - \Lambda_v'}$$

EXPERIMENT

Determine the degree of hydrolysis of aniline hydrochloride in aqueous solution at 25° C.

Procedure.   Make a solution (say $N/32$) of aniline hydrochloride in water.   Place 20 ml of this solution in a conductivity cell and determine the conductivity at 25°.   Dilute the solution with water to $N/64$ and $N/128$, as described on p. 208, and determine the conductivity at each dilution.   Make now a solution of aniline hydrochloride, not in pure water, but in an $N/32$-solution of aniline, and determine the conductivity at the same dilutions as before, the dilution of the original solution being carried out with the $N/32$-solution of aniline.   From the conductivities so determined, calculate the degree of hydrolysis of aniline hydrochloride at each of the dilutions, the equivalent conductivities of hydrochloric acid at $V = 32$, 64, and 128, being taken as 393, 399, and 401 respectively.

Calculation.   From the value of the degree of hydrolysis found calculate the affinity constant of aniline, assuming the ionic product of water at 25° to be $1·02 \times 10^{-14}$.

Rate of reaction, solution, diffusion, etc.   If a reaction in solution involves the formation or removal of electrolytes, or even a change in the number or type of ions present in the solution, the rate of the reaction can often be followed very conveniently by consecutive measurements of the conductance of the solution. Examples are the rate of hydrolysis of esters (see pp. 304–7 for an experiment) or esterification of alcohols, and the rate of ion exchange between a salt solution and an ion-exchange resin (the exchanging ions having different mobilities).   The rate of diffusion of salts in water can also be determined from the rate of change of resistance exhibited between electrodes placed in the diffusion column.[1]

Conductimetric titrations.   Measurements of the electrical conductance can also be employed in order to determine the end-point

of reactions between electrolytes, e.g. neutralization of acids and alkalis, precipitation reactions, etc. The method is of especial value for coloured or turbid solutions, in which the change of colour of an indicator would be more or less masked, or with very dilute solutions, or for reactions for which no convenient indicator is available.

Acid-alkali titrations. When a strong acid is added to an alkali, the conductance of the solution will decrease owing to the disappearance of the hydroxide ion, and its replacement by the less mobile anion of the acid; but when all the hydroxide ion has been removed, by combination with hydrogen ion from the acid added, then any further addition of acid will cause the conductance to increase, owing to the addition to the solution of free hydrogen ion. Since the hydrogen ion has a much greater mobility than any other ion, the presence of a slight excess of free acid will cause a
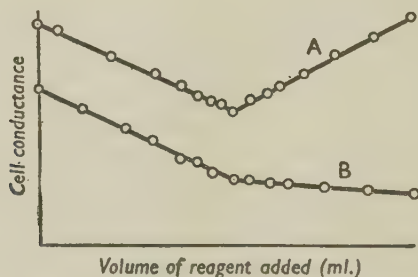
Fig. 10.10. Determination of the equivalence point in conductimetric titrations.
A. Titration of strong base with strong acid.
B. Titration of strong base with weak acid.

marked increase in the conductance. When, therefore, the conductance of the solution is plotted against the number of millilitres of acid added, a curve of the form shown in Fig. 10.10 is obtained. The point of intersection of the two curves gives the number of millilitres of acid required to neutralize exactly the solution of the alkali.

When both acid and alkali are strong, one may carry out the titration from either side; the acid may be added to the alkali, or the alkali to the acid. In the latter case, there is first a diminution of the conductance owing to the replacement of hydrogen ion by a less mobile cation, and then, after the neutral point has been reached, an increase in the conductance, which is sharply defined owing to the fact that OH⁻ is also a highly mobile ion.

When, however, the acid is weak, it is necessary to add the acid to the alkali (*and in this case a strong alkali must be chosen*), and not the

alkali to the acid. If the alkali is added to a weak acid, the mini-
mum is not sharp owing to the fact that the change in conductance
is due not so much to the disappearance of the fast-moving hydrogen
ion (which is present in comparatively small concentration), as to
the replacement of the un-ionized acid molecules by the ions of the
salt formed. When, however, the acid is added to the alkali, the
hydroxide ion is replaced by the much slower anion of the acid, and
a consequent diminution of the conductance of the solution is pro-
duced. As the acid is, however, only slightly ionized, and the
ionization is further reduced by the presence of the neutral salt, the
addition of excess of acid does not, in general, lead to an increase of
the conductance, but only to a sharp change in the direction of the
conductance curves, as shown in the lower graph in Fig. 10.10.

Strong acids, also, may be titrated in presence of weak acids, and
the basicity of an acid may be determined.

Other electrolytic reactions. The conductimetric method of titra-
tion may also be used to determine the end-point of many other types
of electrolytic reaction.[2] Thus, in the reactions

$$NaCl + AgNO_3 = AgCl + NaNO_3$$
$$CH_3.COONa + HCl = CH_3.COOH + NaCl$$
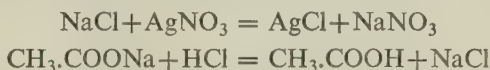
the conductance of the solution remains almost unchanged on addi-
tion of the silver nitrate or of the hydrochloric acid, because the
conductance of sodium nitrate is similar to that of sodium chloride,
and the conductance of sodium chloride is similar to that of sodium
acetate. When, however, excess of silver nitrate or of hydro-
chloric acid is added, the conductance shows a sudden increase.
In the reaction $MgSO_4 + Ba(OH)_2 = Mg(OH)_2 + BaSO_4$ the re-
sultants are both sparingly soluble and separate out from the
solution. There is therefore a marked decrease of the conductance.
On adding excess of barium hydroxide, the conductance rapidly
increases.

Practical procedure. A known volume of the solution to be tit-
rated is pipetted into a suitable conductivity cell. The dipping type
shown in Fig. 10.7 (c) will be suitable for many dilute solutions
and can be immersed in a small beaker. For solutions of about
$N/20–N/100$ it is better to use a similar cell with smaller elec-
trodes; a pair of platinum wires (platinized), about half an inch in
length and sealed into glass tubes containing a little mercury, are
suitable. If the solutions are at room temperature it will not be
necessary to place the cell in a thermostat for the titration unless the
end-point happens to be rather indistinct. The resistance of the
cell may be determined in the usual manner. The titrating solu-
tion is then run in from a burette in small quantities at a time, and

after each addition the solution is well mixed and the resistance
redetermined. To avoid the disturbing effects due to dilution, the
concentration of the titrating solution should be five or ten times
greater than the concentration of the solution to be titrated, the
titrating solution being delivered from a microburette graduated
to 0·01 ml. A graph is drawn of resistances against millilitres of
titrating solution added, and the point of intersection of the curves
gives the equivalence point.

Simplified apparatus. Conductimetric titrations can be greatly
simplified and expedited either by replacing the Wheatstone bridge
telephone detector by a self-contained conductance meter with
visual balance indicator (*see below*), or simpler still, by measuring
the current which passes through the cell when a constant a.c.
voltage is applied to it. A suitable circuit is shown in Fig. 10.11.
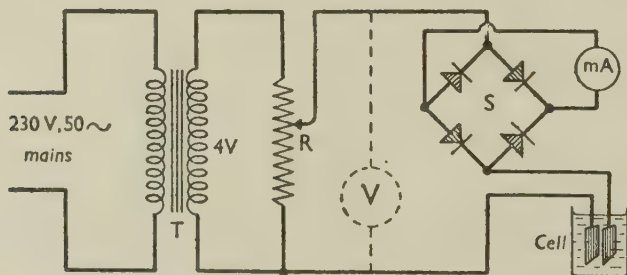
FIG. 10.11. Simplified apparatus for conductimetric titrations, using 50-cycle
source and rectified d.c. milliammeter.

Since high accuracy is not demanded, 50 cycle a.c. is used. The
a.c. mains are connected to the primary of a common step-down
filament transformer T furnishing 2, 4 or 6 volts on the secondary,
and this is further reduced by a variable potential divider R, con-
sisting of an ordinary radio "potentiometer" of about 1,000 Ω.
The current that passes through the conductance cell is registered by
an inexpensive 0–1 or 0–5 moving-coil milliammeter, δ, the current
being rectified by a small selenium instrument rectifier, S (Westing-
house, 5 mA). If the mains voltage fluctuates excessively, one can
adjust R before each reading to keep a constant applied voltage, as
indicated by an a.c. voltmeter, V. More elaborately, the voltage
can be stabilized by interposing a constant voltage transformer or
neon tube or barretter circuit between T and the mains.[3]

An important advantage of this method of following changes of
conductance is the convenience of merely taking a needle reading.
The reading is approximately proportional to the conductance. A

graph of needle reading against ml of titrant therefore gives the required equivalence point.

The sensitivity of the circuit is varied by changing the applied voltage by means of R. A preliminary approximate titration is required, using a low voltage, in order that an optimum range of current can be selected for the principal titration. If necessary the sensitivity of the circuit for small changes of conductance can be enhanced by using a differential method—for example, by using the milliammeter and rectifier to measure only the out-of-balance current in a Wheatstone bridge circuit initially balanced to zero
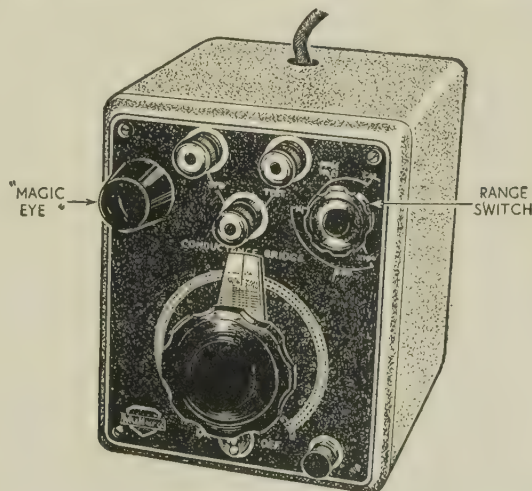
Fig. 10.12. Conductance meter with visual balance detector.
(Courtesy Messrs. Mullard Ltd., London)

current, or by "backing off" the bulk of the current by an auxiliary d.c. voltage.[4]

The Mullard conductance meter. This commercial instrument (Fig. 10.12) has a self-contained Wheatstone bridge circuit with 1,000-cycle oscillator and "magic-eye" bridge balance detector. It is capable of measuring conductances ranging from 1 to 10^{-6} mho with an accuracy of about 1–2%, and is therefore a convenient substitute for the precision bridge for many of the applications of conductance mentioned above.

EXPERIMENTS

Titrate the following solutions conductimetrically:

(1) 50 ml of $N/100$ NaOH with N HCl from a microburette, (2) 50 ml of $N/100$ Na_2CO_3 with N HCl, (3) 50 ml of $N/50$ Na_2SO_4 with N $BaCl_2$.

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TRANSPORT NUMBERS AND ELECTRODE PROCESSES

11A. TRANSPORT NUMBERS

Introduction

When a current of electricity is passed through an electrolyte, the change of concentration at the electrodes is, in general, not the same. Although equivalent amounts of positive and negative ions are necessarily discharged at the electrodes (Faraday's Law), the velocity with which the ions move in the potential gradient is different. Consequently, the amount of electricity carried by cations in one direction is different from that carried by anions in the other direction. These two amounts are, indeed, in the ratio of the velocities of migration (mobilities) of the cation and anion, u_+ and u_-, respectively. It is of interest to mention that in the extreme case of certain ionic *crystals* (e.g. silver chloride) only one of the ions can move through the lattice and therefore carries *all* the current. In solution, however, both ions can move, but their velocities differ because of their different (hydrated) radii.

The total current passing through a solution under a given potential is proportional to the sum of the ionic mobilities, $(u_+ + u_-)$. The cation carries a fraction equal to $u_+/(u_+ + u_-)$ and the anion $u_-/(u_+ + u_-)$. These fractions are called the *transport (or transference) numbers* of cation (t_+) and anion (t_-), and clearly $t_+ + t_- = 1$.

The relationship between transport numbers and ionic mobilities is readily derived, as follows. If an ion at concentration c g equiv. per litre has a transport number of t, and the specific conductivity of the solution is κ ohm^{-1}cm^{-1}, then in a unit cube of solution subjected to a potential gradient of 1 V per cm, a current of κ amp would flow. The quantity of electricity transported by the given ions in 1 second would therefore be $t \times \kappa$ coulombs, which corresponds to $t\kappa/96{,}500$ g equiv. The solution contains $c/1{,}000$ g equiv. per ml, and therefore the rate of migration of the ions, u, is given by $u = \dfrac{1{,}000 t\kappa}{96{,}500c}$ (cm per second).

Transport numbers can be determined by (a) measurement of the quantity of electrolyte transported to the cathode or anode during electrolysis (Hittorf's method, 1853), or (b) by measurement of the rate of movement of a boundary between two electrolytes during

electrolysis (Lodge 1886, Whetham 1893), or (c) in certain cases, from measurements of e.m.f. of concentration cells with and without transport (as described in Ch. 12, pp. 293–4).

Hittorf's method.   In this method one measures the total quantity of electricity passed through a cell and the amount of one of the ions which has passed away from (or into) the space around one of the electrodes.   It is assumed that the change of concentration takes place only in the neighbourhood of the electrodes, and that the intermediate portion of the solution remains unaltered.   It is convenient, therefore, to have an apparatus such as that shown in Fig. 11.5 (p. 226), in which the anode region, cathode region, and intermediate region are well separated so that the solutions can be withdrawn from the sections separately after electrolysis and analyzed.   It is evident that too great a quantity of electricity must not be passed through the cell. Further, the current must not be, on the one hand, too intense, as that might cause heating and mixing by convection, or, on the other hand, so feeble that diffusion could partially annul the concentration changes produced by electrolysis.

Hittorf's method, although simple in principle and widely applicable, suffers from the experimental disadvantage that it depends on measuring small *changes* of concentration, and therefore very accurate analytical methods must be employed if reliable values of the transport number are to be obtained.

Moving boundary method.   A sharp boundary is formed in a tube between solutions of two salts having a common ion (say, A^+X^- and B^+X^-, Fig. 11.1).   It must be possible to observe the position of the boundary by having A and B of different colour, or by having an indicator substance in the solutions or by an optical method depending on a difference of refractive index or ultra-violet absorption spectrum between the two solutions.   If now a potential gradient is set up along the tube by connecting a battery to electrodes situated at the ends of the tube, current will flow by migration of the cations towards the cathode and anions towards the anode.   At the boundary the A^+ and B^+ ions will move in the same direction and hence the boundary will be observed to move.   In general A^+ and B^+ ions will not move at the same rate.   Suppose the cathode is situated in the AX solution.   If B^+ ions move faster than A^+ ions, they will overtake the latter and pass them, causing the boundary to become more and more diffuse.   If, on the other hand, the A^+ ions are the faster, they

FIG. 11.1. Basis of the moving boundary method for determining transport numbers (see text).

will tend to move away from the B^+ ions at the boundary. Of course, a separation of ions cannot occur to any appreciable extent, but the effect prevents the A^+ and B^+ ions from mixing by diffusion. The result is the formation of a self-sharpening boundary *aa* which migrates along the tube with a velocity equal to that of the *faster* ion (A^+), and therefore the experiment leads to a value for the transport number of A^+ in the solution of A^+X^- (concentration $= c$ g equiv. per litre). The tube is graduated so that the volume, V ml, swept through in time t seconds during the passage of Q coulombs of electricity can be determined. The amount of current carried by A^+ ions across any section *bb* in the AX solution is clearly equal to the number of g equiv. of A^+ ions which would have passed that section (namely, $c \times V/1,000$) multiplied by the charge (in coulombs) carried by each g equiv. (namely, 1 Faraday $= 96,500$ coulombs). Hence, the fraction of the current carried by A^+ ions ($= t_+$) is given by $t_+ = \dfrac{cV \times 96,500}{1,000 \times Q}$. c is known from the original concentration of AX solution, and V and Q are measured during the experiment. The moving boundary method is therefore a direct one, and is capable of high accuracy.

In carrying out a moving-boundary determination, the following conditions must be observed. (1) A suitable "following ion", B^+, must be employed, having a mobility less than that of A^+. (2) The conductance of the "indicator" solution should be slightly less than that of the leading solution. (3) The denser solution must be the lower one in the tube, to obviate mixing. (4) The current of electricity passed through the tube must not be so large as to cause appreciable heating, expansion and convection of the liquid. An obvious precaution is to keep the tube fairly narrow and immerse the apparatus in a bath of water. (5) As there must be no *flow* of liquid along the tube, one end of the apparatus must be closed, and a non-gassing electrode must be employed at this end. These conditions are met in the experiment described below (p. 228). Another technique sometimes applicable is the "autogenic boundary" device of Franklin and Cady [1]; the "indicator" solution is produced *in situ*—for example, by the anodic solution of cadmium, giving $CdCl_2$.

Concentration of following ion. While the boundary is moving, the theory given above for the A^+ ion must also hold for the B^+ ion, and hence $t_{A^+}/c_{A^+} = t_{B^+}/c_{B^+}$. It appears therefore that the "indicator" solution must be of exactly the right concentration if the experiment is to succeed, and that one must know t_{A^+}/t_{B^+} *a priori* to arrange c_{A^+}/c_{B^+}. In practice, however, the concentration of the "indicator" solution is not highly critical as it automatically adjusts itself in the

neighbourhood of the boundary, so that t_{A^+}/t_{B^+} need only be known approximately (within 10%). If BX is the lower solution, it should be made slightly *more* concentrated than the value of c_{A^+} calculated from the above equation so that the density changes near the boundary during electrolysis do not cause convection. If the "indicator" solution is *above* the leading solution, then it should be *less* concentrated than that calculated.

Measurement of quantity of electricity. The simplest method of measuring the quantity of electricity passed during a transport number determination is by means of a reliable milliammeter (or millivoltmeter shunted by adjustable resistance box) in series with the apparatus. If the current changes slowly, one can note the reading at frequent intervals and calculate the total electricity passed by graphical summation of current × time. Alternatively, the area under the current–time graph can be computed by Simpson's Rule. For greater accuracy, the milliammeter can be replaced by a standard resistance, and the potential across it determined by an accurate potentiometer (p. 247). The value of the resistance should be chosen to suit the full range of the potentiometer; for example, if the current is 10 mA, the potential drop across a standard 100-ohm resistance would be 1 V, and this could be determined to better than 1 mV.

In determinations by the moving-boundary method it is convenient to maintain a *constant current* through the apparatus so that the boundary moves at constant velocity. Errors in the current–time integration are thereby reduced. The resistance of the cell increases during the measurement and hence the current tends to fall. For work of moderate accuracy the current can be regulated by manual adjustment of a rheostat (preferably a large one with rotary adjustment) used as potential-divider across the supply voltage. Numerous electronic circuits have been devised for current-control; that used by Hartley and Donaldson [2] in connection with their moving-boundary apparatus is particularly simple and effective though a high voltage may be required.

In determinations of transport numbers by Hittorf's method it is traditional to use a *coulometer* for measuring the quantity of electricity passed. This is particularly suitable since only one value of Q is needed and a coulometer gives the integrated number of coulombs directly irrespective of changes of current. The silver or iodine coulometers are capable of giving very high accuracy, the electrolytic-gas coulometer is sensitive and accurate to 05·%, but the copper coulometer, formerly much used, is rather less satisfactory, and has nothing but cheapness to recommend it.

The silver coulometer. A convenient form of apparatus is shown

in Fig. 11.2. A glass or porcelain crucible, a, having a porous base of No. 2 or 3 porosity is supported inside a small beaker by a glass tripod, b, so that its base is clear of the bottom of the beaker. The cathode, c, is a sheet of platinum foil, about 1 sq. cm in area, with a platinum wire welded to it. The crucible + cathode are cleaned, washed, and dried to constant weight in an oven at $150°$ C before the experiment. The usual precautions of

cooling for sufficient time in a desiccator must, of course, be observed. The anode, d, is a coil of stout silver wire (or a piece of silver foil with wire attached). Both electrodes are connected by small brass connections, e. The electrolyte is approximately 15% $AgNO_3$ solution; the $AgNO_3$ should be very pure, and in particular, free from organic matter. The current passed through the coulometer should not exceed 10 mA per sq. cm of cathode surface. After the electrolysis, the cathode

Fig. 11.2. Convenient form of silver coulometer.

is carefully disconnected and left in the crucible, together with any loose crystals of silver. The crucible is lifted out of the beaker with platinum-tipped tongs and carefully washed externally with a jet of water and then internally with suction in the usual manner until the washings give no reaction for silver. The crucible
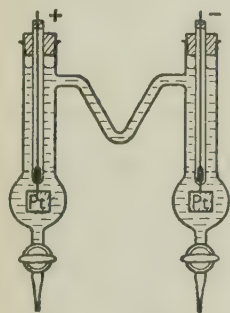
Fig. 11.3.
Iodine coulometer.

and contents are then dried to constant weight at $150°$, cooled in a desiccator and weighed again. The accuracy obtainable with this coulometer will generally be limited only by the accuracy of weighing. 1 coulomb deposits $0 \cdot 001118$ g of silver.

The iodine coulometer. The apparatus is shown in Fig. 11.3. The electrodes are platinum foils. The electrolyte *in the bulb* of the anode compartment is concentrated KI solution; that around the cathode is a concentrated solution of I_2 in KI. The upper parts of the apparatus contain 10% KI solution. During electrolysis iodine is formed at the anode and consumed at the cathode. After electrolysis the anode solution is run off and titrated for iodine in the usual way.

The copper coulometer. This is suitable only for approximate work, as rather elaborate precautions (exclusion of air, cooling to $0°$ C, use of two coulometers simultaneously with different electrode areas) [3] are needed to get results of high accuracy. The electrodes are sheets of pure copper,

and the electrolyte consists of 125 g of copper sulphate crystals, 50 g conc. H_2SO_4, 50 g ethanol, made up to 1 litre with distilled water. Before use the cathode is cleaned in dilute nitric acid, washed with water and alcohol, dried in a steam oven, cooled in a desiccator, and weighed

FIG. 11.4. Electrolytic-gas coulometer.

accurately. A stream of CO_2, N_2 or H_2 is passed through the electrolyte before and during electrolysis to reduce the oxygen content of the solution. A current density of about 10 mA per sq. cm is suitable. After electrolysis, the cathode is rinsed with water and alcohol and dried and weighed as before. 1 coulomb deposits $0·329_4$ mg of copper.

The electolytic-gas coulometer. The volume of electrolytic gas produced by the electrolysis of water which has been rendered conducting by addition of 10% $K_2Cr_2O_7$ or Na_2SO_4 is measured. An apparatus such as that shown in Fig. 11.4 is convenient. *A* is the electrolysis cell. Current is passed for some time before the experiment to saturate the liquid. The apparatus is then connected and tested for leaks. *B* is a microburette containing mercury, which is run out until the pressure in the apparatus is exactly equal to that of the atmosphere, as shown by the manometer *C*. The current is then passed. *B* is readjusted, and the amount of mercury run off is determined either volumetrically or by weight. 1 coulomb produces $0·174$ ml of gas (corrected to N.T.P., and for water vapour).

The electrolytic-gas coulometer is therefore suitable for measuring rather smaller quantities of electricity than the other coulometers described.

EXPERIMENT

Determine the transport number of Ag^+ in a solution of silver nitrate by Hittorf's method.

The type of apparatus traditionally used for determinations by Hittorf's method is shown in Fig. 11.5. *A*, *B*, and *C* are the cathode, anode, and intermediate compartments. The electrodes consist of stout silver wires, cemented

FIG. 11.5. Apparatus for determination of transport number of silver nitrate by Hittorf's method.

into glass tubes by means of wax, and soldered to copper leads inside the tubes. The whole apparatus is filled with a solution of silver nitrate, about $N/20$, made up accurately *by weight*. As

the solution in the cathode compartment becomes more dilute during electrolysis and is therefore liable to undergo mixing by convection, one can insert a thin *loose-fitting* disc of rubber or cork, *a*, to minimize this effect. The screw-clips, *b*, are applied only at the end of electrolysis to isolate the three compartments. The apparatus should be protected from direct sunlight or heat which might cause convectional mixing.

A current of about 10–20 mA is suitable. A potential of about 30–40 V is required (depending on the dimensions of the apparatus), and can be obtained from batteries, a rectifier, or d.c. mains with variable resistance. It is convenient to have a 0–50 milliammeter in series with the apparatus, but the quantity of electricity passed is usually measured by a coulometer. The copper coulometer (see above) is the simplest, and is accurate enough for this experiment, but any of the other methods of measuring the number of coulombs (as described above) may be employed.

About 100 coulombs are passed through the cell (2–3 hours at 10 mA), and then the clips *b* are applied and *A*, *B*, and finally *C* are drained into separate, dry, weighed flasks. Each compartment is rinsed with a little of the original solution, the rinsings being added to the appropriate flask. The flasks are then weighed, and their contents titrated with standard $N/20$ potassium thiocyanate solution, using ferric alum as indicator. (Alternatively, the silver may be determined gravimetrically or by electrometric titration with KCl solution.[4]) The analysis must be made as accurately as possible. The composition of the intermediate compartment, *C*, should be found identical with that of the original solution; if it has changed, the current has been passed too long, and the experiment must therefore be repeated for a shorter time.

Calculation. Let Q be the number of coulombs passed through the apparatus. Consider the processes occurring in the anode compartment. Suppose the initial concentration of *silver* in the solution was w g per 1,000 g of *water*. Let the amount of Ag found by analysis after electrolysis be w' g in W g of *solution*. The anolyte after electrolysis therefore consisted of w' g of Ag $+ (W - w')$ g of water. If no concentration changes had taken place, this quantity of water would have contained $w \times (W - w')/1,000$ g of Ag. There has therefore been a gain of silver equal to $w' - w(W - w')/1,000 = X$ g. This increase is the net result of a gain by solution of the anode and loss by migration of Ag$^+$ out of the anode compartment. By Faraday's Law, the amount of silver dissolved at the anode must be $Q \times 107 \cdot 88/96,500 = Y$ g. Hence, the amount that has migrated away is $(Y - X)$ g. This amount has therefore carried a fraction of the current given by $(Y - X)/Y$, which is therefore the transport number of the silver ion, t_{Ag^+}, in the AgNO$_3$ solution.

The calculation for the cathode compartment is entirely analogous, and should, of course, lead to the same value of t_{Ag^+}.

EXPERIMENT

Determine the transport number of H^+ *in* HCl *solution by the moving-boundary method.*

A simple form of moving-boundary apparatus is shown in Fig. 11.6. A sharp boundary is produced by means of a stopcock, A, as described later. The boundary is caused to move down the tube BC, which consists of half of a 1 ml pipette, graduated in 0·01 ml. The cathode, F, is a silver–silver chloride electrode of considerable capacity so that no gases are evolved, the electrode reaction being $AgCl + \ominus \rightarrow Cl^- + Ag$. The electrode is constructed from platinum
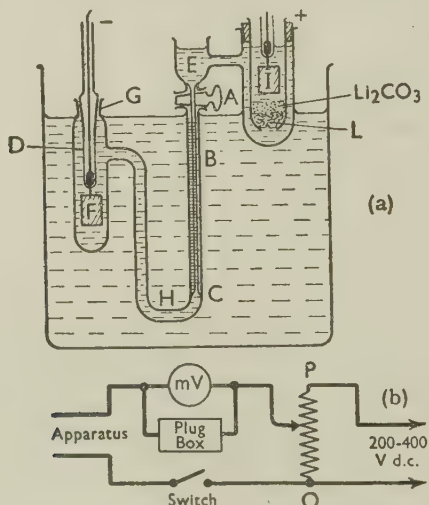
FIG. 11.6. Apparatus for determination of transport number of HCl by the moving-boundary method.
(a) Glass cell.   (b) Circuit diagram.

gauze attached to a platinum wire sealed in the glass tube D; the gauze is first electroplated with silver which is then chloridized by being made the anode in conc. HCl. The cathode compartment is sealed by a greased ground glass joint, G. The "indicator solution" in compartment E consists of LiCl, and the anode is a platinum foil electrode, I, which is placed inside a tube containing some solid Li_2CO_3 (retained in position by a plug of glass wool, L). The object of this arrangement is to ensure that no hydrogen ions escape from the neighbourhood of the anode.

A current of about 2–5 mA produces a convenient rate of movement. A potential of 100–400 V is needed, and may be obtained from batteries or d.c. mains or both. The current is best measured

by an accurate 0–100 millivoltmeter shunted by a standard adjustable resistance box, and it is convenient to maintain a constant current during the experiment by manual adjustment of a large sliding rheostat, PQ, of about 5,000 Ω, used as a potential divider. The circuit is shown in Fig. 11.6 (b). (Electronic current-stabilization may be used instead of manual adjustment, if desired.)

Procedure. Prepare a litre of approximately $0.1N$ HCl, and add to it sufficient solid methyl orange to give it enough colour to be seen in the moving boundary tube. Standardize this solution accurately by titration with standard alkali or borax. Take a portion of the solution and add to it solid Li_2CO_3 a little at a time, allowing each lot to dissolve before adding the next, until the solution is just definitely yellow. A slight excess is permissible, but too much would make the LiCl solution so prepared too dense. The concentration of this LiCl indicator solution must be adjusted approximately to conform to the relation $(t_+)_{HCl}/c_{HCl} = (t_+)_{LiCl}/c_{LiCl}$. Since $(t_+)_{HCl}$ is roughly 0·8, and $(t_+)_{LiCl}$ is about 0·3, the theoretical concentration of LiCl must be about $0·1 \times 0·3/0·8 = 0·04$. For reasons explained above, a slightly less concentrated solution is preferable. The $0·1N$ LiCl should therefore be diluted with about three times its own volume of distilled water.

The apparatus is first cleaned and rinsed twice with the HCl solution. It is then entirely filled with the HCl solution, and the stopper G is inserted and the stopcock A is closed. The bore of the stopcock will therefore contain HCl. The HCl is then poured off from vessel E, and this part of the apparatus is rinsed with water and then filled with the LiCl solution. Particular attention must be given to see that the section of tube immediately above stopcock A is well rinsed with LiCl solution; this part can be washed out with the aid of a glass tube drawn out to a fine jet. The anode assembly is then inserted, as shown. The whole apparatus is set up in a glass-sided tank of water to prevent disturbances of the boundary by temperature change. (The vessel D would act like a thermometer.) The electrical circuit is wired up, and checked for polarity.

To form the boundary, the stopcock A is turned very slowly until fully open. The current should then be switched on at once. In order to ensure that the delicate millivoltmeter is not subjected to excessive current, the current should be started with *all* the plugs in the box; they can then be taken out one at a time, starting with the 1 ohm plug until the millivoltmeter deflection is almost full-scale. During the experiment the resistance of the cell increases because HCl in the tube BC is gradually replaced by LiCl which has a lower conductivity. It is therefore advisable to begin the experiment with the sliding contact of the potential divider about half way across

PQ so that it can be advanced gradually towards *P* to maintain a constant reading on the millivoltmeter as the experiment proceeds. (Alternatively, the rheostat may be dispensed with and the current read at frequent intervals.)

The boundary—yellow above, red below—should be very sharp. It can be seen best by placing a thin sheet of white paper behind the apparatus and an electric light bulb behind the paper.   As soon as the boundary reaches the first graduation on the tube *BC*, a stop-clock should be started, and subsequently the time should be noted (without stopping the clock) when the boundary reaches each graduation down to the bottom of the tube.

Calculation.   Plot a graph of volume reading on the tube *BC* against time.   If the current has been kept constant, this graph should be a straight line, as the theory of the method (p. 222) gives the equation $t_+ = \dfrac{F \cdot c \cdot V}{1{,}000 \ Q}$ (*c* = conc. of HCl in g equiv. per litre, *V* = volume in ml swept through by the boundary during the passage of *Q* coulomb = current in amp × time).   Draw the best straight line through the points and work out the mean rate of movement of the boundary, $\overline{V}$, in ml per second.   The current can be calculated as follows.   If the resistance of the millivoltmeter is *R* ohms and that of the shunt employed is *R′*, the net resistance of the two in parallel is $RR'/(R+R')$; hence, if the needle reading had been maintained at *M* millivolts, the current flowing, *I*, by Ohm's Law must have been $\dfrac{M}{1{,}000} \cdot \dfrac{(R+R')}{RR'}$ amp.   Hence, applying the above equation for the movement produced in 1 second, $t_+ = 0{\cdot}001 \ Fc\overline{V}/I$, from which t_+ can be obtained.   (If the alternative procedure is followed in the experiment, i.e. constant voltage, changing current, one can plot a graph of current against time and evaluate the quantity of electricity, *Q*, as the area under the curve.   This calculation should be applied to several sections of the results to ascertain whether the ratio of V/Q was the same throughout.)

The small correction for volume change at the Ag–AgCl electrode, and the correction for movement of solvent necessary to make transport numbers determined by the moving boundary method strictly comparable with those obtained by the Hittorf method, can be neglected in the present instance.[5]

BIBLIOGRAPHY 11A: Transport numbers

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[3] Richards, Collins and Hermrod, *Proc. Amer. Acad.*, 1899–1900, **35**, 123.
[4] MacInnes and Dole, *J. Amer. Chem. Soc.*, **53**, 1357.
[5] cf. Robinson and Stokes, *op. cit.*

11B. ELECTRODE PROCESSES

Introduction

When dilute sulphuric acid is electrolyzed with platinum electrodes, the net reaction is the decomposition of water with liberation of hydrogen at the cathode and oxygen at the anode. Since the reaction

$$H_2O(l) \rightarrow H_2(g, \text{1 atm}) + \tfrac{1}{2}O_2(g, \text{1 atm})$$

is accompanied by an increase of free energy of 56·6 kcal, this is the *minimum* amount of electrical energy theoretically capable of causing the reaction to proceed in a *reversible* manner. Rather more energy is needed to produce electrolysis at a finite rate. Since $\Delta G = -zEF$ (p. 239) and $z = 2$ for this reaction, it follows that *at least* 1·23 V must be applied. In practice, about 1·67 V is needed to effect
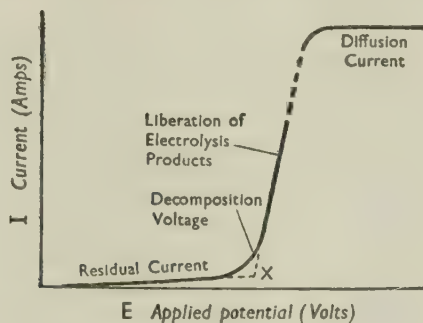
FIG. 11.7. Current-voltage curve for electrolysis.

electrolysis of $N\,H_2SO_4$ with smooth platinum electrodes because the electrodes are not "reversible". At lower voltages no gas is evolved, and very little current passes through the cell, as shown diagrammatically in Fig. 11.7. The point X is called the *decomposition voltage* (or potential). The small current that flows at applied voltages below X is the *residual current*. It is associated with formation *in solution* of small quantities of hydrogen and oxygen which diffuse away from the electrodes or, in the case of hydrogen, react with dissolved oxygen. When a potential (less than X) is first applied to the electrodes, a relatively large current passes momentarily, but it quickly falls off to the small value indicated in Fig. 11.7. The cell is then said to be *polarized*. Polarization is caused by accumulation of the products of electrolysis at the surface of the electrodes with the result that the system constitutes a voltaic cell with a *back e.m.f. of polarization* which opposes the applied voltage. If no mechanism

existed for removal of polarization products, zero current would then pass.   On the other hand, the residual current can be increased by stirring the solution to assist removal of these substances. Similarly, if easily oxidizable or reducible substances (e.g. Fe^{++}, Fe^{+++}) are added to the cell, a progressive electrode reaction can take place with consequent increase of current; this phenomenon is *depolarization* of the electrodes.

When polarization is due solely to accumulation of substance in the neighbourhood of the electrodes it is called *concentration polarization*.   Another type of polarization is observed when a gas such as H_2 or O_2 would be the product of electrolysis; a potential markedly greater than the reversible potential must be applied before any gas is liberated.   This is the phenomenon of *overvoltage*.   Its origin is still controversial, but its practical importance is extensive.
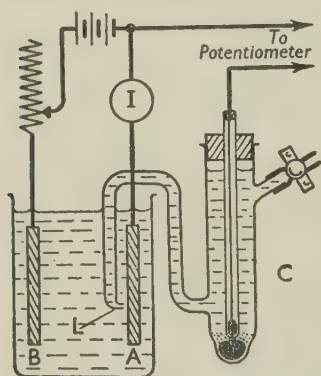
FIG. 11.8. Determination of the potential of an electrode during electrolysis.

For example, the overvoltage of hydrogen on *smooth* platinum is about 0·09 V and that of oxygen about 0·4 V; this is why the decomposition voltage of water is 1·67 V instead of the reversible value of 1·23 V.   With a lead or mercury cathode it would be considerably higher because the hydrogen overvoltages of these metals are high. In contrast, the decomposition voltage of HCl with platinized platinum electrodes is close to the reversible value because both H_2 and Cl_2 show negligible overvoltage on platinized platinum.   Overvoltages are not easily reproducible as they depend greatly on electrode structure, on current density, and on traces of impurities.

As polarization of a cell is the sum of the independent polarization of the two electrodes, it is more informative to study the current-potential curves for each electrode separately rather than that for the cell as a whole.   The arrangement shown in Fig. 11.8 is used. While a current I is being passed through the cell, the potential of the electrode A *with respect to the adjacent solution* is measured by means of a calomel electrode C and potentiometer.   (See Ch. 12.) The calomel vessel has a special form with a tip, L ("Luggin capillary") which can be brought close to the electrode surface so that the measured potential is not complicated by the potential drop ($I \times R$) which necessarily exists between the two electrodes A and B while a current is passing.   This arrangement permits the

determination of *discharge or deposition potentials*, i.e. for single electrode processes.

When a potential greater than the decomposition voltage is applied to the cell, electrolysis takes place at a rate which increases rapidly with increase of potential (Fig. 11.7). A limit is set only by the rate at which the proper ions can get to (or the products get away from) the electrode. At relatively high potentials (easily reached with small electrodes and very dilute solutions) the *limiting current (diffusion current*, Fig. 11.7) becomes constant, independent of potential, because the overall rate is controlled by diffusion. The magnitude of the diffusion current is proportional to the concentration of substance which takes part in the electrode reaction. This fact provides the basis of *polarography*, a valuable method of analyzing solutions by determination of current–potential curves with a minute platinum electrode or (more often) a dropping-mercury electrode.

Many practical electrode processes are, of course, complicated by secondary reactions (e.g. sulphate $\rightarrow$ persulphate, $2Hg + 2Cl^- \rightarrow Hg_2Cl_2$). However, the only other phenomenon that need be mentioned here is that of *passivity*. Fe, Co, Ni, Cr, Mo, W, etc. are metals which will dissolve anodically in dilute HCl provided they are in the *active* condition, but if made the anode in H_2SO_4, HNO_3, etc., they are liable to become *passive* and then subsequently behave as unattackable electrodes. Passivity is due to the formation of a thin, coherent oxide film which is impermeable to the metal ions. The metal can be restored to the active condition by scraping off this film or removing it cathodically or with hot HCl.

EXPERIMENT

Determine current–voltage curves with the following electrodes and electrolytes.

   (1) Two platinized platinum electrodes in (a) $0.1N$ H_2SO_4, (b) $0.1N$ Na_2SO_4, (c) $0.1N$ $ZnSO_4$, (d) $0.1N$ $CuSO_4$;
   (2) Lead cathode, platinized platinum anode, in $0.1N$ H_2SO_4;
   (3) Nickel anode, platinized platinum cathode in $0.1N$ H_2SO_4.

Details. This experiment can be performed with the simple apparatus shown in Fig. 11.9, but if desired, the superior technique illustrated in Fig. 11.8 may be used. The electrodes should consist of 1 cm squares of stiff foil, bearing a stout wire by which they can be mounted about 2 cm apart in a small beaker of the solution. The platinum should be freshly platinized (p. 206), the lead scraped with a knife, and the nickel made active by cleaning with hot conc. HCl and treatment as cathode in dilute H_2SO_4.

The milliammeter (Fig. 11.9) should be provided with a shunt to enable it to be read up to about 0·1–0·2 amp. Potentials up to about 3 V will be needed. The voltmeter V should be of high resistance so that the current passing through it is small, but a preliminary series of amp–volt readings should be taken with no solution in the cell to determine the correction to be applied.

First observe with cell 1 (a) the rapid fall of current on switching on, and by disconnecting the battery verify the existence of a back e.m.f. which also rapidly decays. Obtain current–voltage curves by increasing the potential in steps of 0·2 V from 0 upwards, allowing two minutes at each stage for the current to assume a more or less steady value before advancing the rheostat for the next potential. Note the potentials at which visible electrolysis commences. Correct the ammeter readings for voltmeter current and the voltmeter readings for IR drop through the cell, and plot the corrected $I–E$ curves. Note the approximate decomposition voltages in each case.

Results. In cell (a) the cathode may be assumed reversible, and the hydrogen discharge potential should therefore be given by $(RT/F)\log_e a_{H^+}$. Since $f_{\pm}$ for 0·1N H_2SO_4 is about 0·4, $a_{H^+} \approx 0·04$, and the reversible discharge potential should be about $-0·08$ V (on the normal hydrogen scale). Hence calculate the discharge potential of oxygen at the anode and compare it with the theoretical reversible value. Since the anode process is the same in experiments 1 (a), (b), (c), (d) and (2), the anode potential at the decomposition point may be assumed the same, thus permitting the cathode

Fig. 11.9. Apparatus for determination of current-voltage curves.

potentials for these cells to be calculated even without measuring them directly by the calomel electrode method. In the cell 1 (b) the cathode potential should be that for discharge of hydrogen from a neutral solution, $[H^+] = 10^{-7}$, but $f_{\pm} = 0·4$ because of the presence of Na_2SO_4.

Since metals are generally deposited with negligible overvoltage, the cathode potentials in experiments 1 (c) and 1 (d) should correspond to the reversible potential. ($E^{\circ}_{Zn} = -0·76$: $E^{\circ}_{Cu} = +0·34$; $f_{\pm}$ for 0·1N $ZnSO_4$ or $CuSO_4 \approx 0·2$.) The difference between deposition potentials of metals is employed in electro-analysis and in polarography.

The difference between the decomposition voltage for 1 (a) and (2) gives the overvoltage for hydrogen on lead.

Experiment (3) shows initial solution of the Ni anode (confirm with dimethylglyoxime), and after a while a decrease of current as the nickel assumes the passive state which is subsequently retained at all potentials.

Solution of Ni ceases (check) and the only electrode process is evolution of oxygen (with overvoltage) as for a platinum electrode (expt. 1 (a)).

It should be understood that "decomposition voltages" are not accurately reproducible quantities since the rate of electrode processes is dependent on many factors.[1]

EXPERIMENT

Investigate the electro-oxidation of potassium ferrocyanide; (1) show that the limiting current is controlled by diffusion, and (2) determine the diffusion coefficient of the ferrocyanide ion.

Procedure.[2] Prepare a large silver–silver chloride electrode (p. 228), to be used as unpolarizable cathode of well-defined, con-
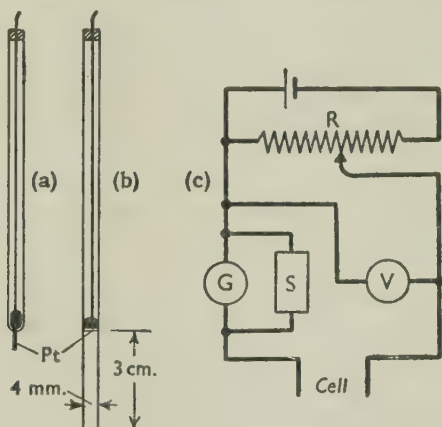
FIG. 11.10. Apparatus for study of diffusion currents at polarized electrodes. (a), (b) Platinum micro-electrodes. (c) Circuit diagram.

stant potential, and two platinum micro-electrodes of the form shown in Fig. 11.10 (a) and (b). The electrical circuit is shown in Fig. 11.10 (c). The voltmeter V should be capable of reading up to 1 V with a sensitivity of 0·01 V. The maximum sensitivity of the galvanometer should be at least 0·1 μA per mm. A 0–10 micro-ammeter can be used, if available. Another method of measuring these small currents is to place a large standard resistance, e.g. 10,000 Ω, in series with the cell and measure the potential drop across it with a potentiometer. The voltmeter reading must then be corrected for the potential drop across the resistance.

Prepare 500 ml of approximately 0·1N KCl solution, and use it to make up 100 ml of solutions 0·01, 0·005, and 0·025 M with respect to potassium ferrocyanide. (1) Determine current–voltage curves for the KCl base solution, and the three ferrocyanide solutions, using

electrode (*a*).   Allow 2 minutes for each reading to become steady, and take readings in steps of 0·1 V up to 1 V.   Draw the (corrected) curves, and note the magnitude of the limiting current (at, say, 0.7 V) for each solution, and show that it is proportional to ferrocyanide concentration.   Verify that the limiting current is increased by stirring the solution near the electrode.   Also, verify by microchemical tests that ferrocyanide is oxidized to ferricyanide.

(2) Electrode (*b*) is designed for measuring the *linear* diffusion of ferrocyanide from the bulk of the solution at the lower end of the tube (where the concentration is supposed constant) to the electrode surface where, during electrolysis, the concentration is zero.   A diffusion gradient is gradually established along the tube.   The ferricyanide solution produced near the electrode has a slightly lower density than the ferrocyanide and therefore tends to keep the column of solution from mixing by convection.

Using the 0·005*M* ferrocyanide solution, determine a current–time curve with a *constant applied potential* of 0·7 V, i.e. follow the change of diffusion current with time.   Start a clock when the current is switched on and take readings every 10 seconds at first, but then at longer intervals as the current steadies off, continuing the readings for about 30 minutes.   Measure the area of cross-section of the tube.

Make similar determinations with the base solution containing KCl only, and subtract these readings from the limiting current values to obtain the current carried by the ferrocyanide only.

Calculations.   Diffusion is controlled by Fick's Law, according to which the flow or "flux" (*f*) of substance across a given plane is proportional to the concentration gradient.   Considering only *linear* diffusion, the position of the plane being denoted by x, the number of moles δN of solute crossing the plane in time δt is given by

$$f = \delta N/\delta t = DA \mathrm{d}C/\mathrm{d}x$$

where D is the *diffusion coefficient* (units cm^2 sec^{-1}), A is the area of cross section of the diffusion column, and $\mathrm{d}C/\mathrm{d}x$ is the concentration gradient along the direction of x.

In the present system, the concentration gradient is changing with time and is not linear along the tube.   It can be shown that if at $t = 0$ the concentration at plane $x = 0$ is suddenly maintained at $C = 0$, then the concentration distribution along a tube, which is long compared with the extent of depletion of the solution, is given by

$$C_{x,t} = C\frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}\mathrm{d}y$$

where C is the original concentration of the solution, y is an integration variable and $z = \dfrac{x}{2\sqrt{Dt}}$.   Now, in the present experiment, the diffusion

current is controlled by the rate at which ferrocyanide arrives at the platinum electrode surface, which is the plane $x = 0$. Every mole arriving accounts for 1 Faraday of current. Therefore, by Fick's Law, the current at time t is given by

$$I_t = FAD\left(\frac{\partial c}{\partial x}\right)_{x=0,t}$$

The gradient near the electrode is obtained by differentiating the above expression. Thus, $\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{C}{\sqrt{\pi Dt}}$ and hence,

$$I_t = FCA\sqrt{D/\pi t}$$

This last expression should represent the change of diffusion current with time. The data can be tested for conformity to the diffusion theory by plotting I_t against $\sqrt{1/t}$ which should give a straight line of slope equal to $FCA\sqrt{D/\pi}$. Hence D can be calculated. (Note that C should be expressed in moles per ml, A in sq. cm, and I in amps.)

For comparison, an approximate value of the diffusion coefficient of an oxidizable or reducible ion in presence of excess of indifferent salt can be deduced from its equivalent conductance at infinite dilution, Λ_0, since

$$D \approx \frac{RT\Lambda_0}{zF^2} \quad \text{(Nernst, 1888)}$$

In the case of the ferrocyanide ion, $z = 4$, and $\Lambda_0 = 110 \cdot 5$ at $25°$.

The dropping-mercury electrode (polarograph). In place of (or in addition to) the above experiments, one may study all the principal electrode phenomena with a dropping-mercury electrode. The apparatus and the theory are more complicated than with a stationary electrode, but the dropping-mercury electrode is used in polarography because it gives a constantly renewed electrode surface, and a reproducible average diffusion current. Also, as the hydrogen overvoltage on mercury is high, electro-reductions can be carried out at very negative cathode potentials. Further, even alkali metals can be deposited because they amalgamate with the mercury.

It is not necessary to have an elaborate recording polarograph, although, of course, this instrument is very advantageous for routine analytical work. Current–voltage curves ("polarograms") can be obtained satisfactorily with the simple electrical apparatus used in the preceding experiment together with an electrode assembly such as that shown in Fig. 11.11.

A is a reservoir containing specially purified mercury. B is a platinum electrode for contact. C is a length of polyvinyl chloride tubing (which is preferable to rubber). The jet D consists of about 7–8 cm of fine-bore thermometer tubing. The apparatus must give a drop-time in dilute KCl of 3–5 seconds. The cell must provide a tube F for bubbling nitrogen to remove dissolved oxygen, and a connection to a satd. KCl calomel electrode I of large capacity.

The cell illustrated in Fig. 11.11 has a sintered glass disc G and agar plug H to separate the test solution in the limb E from the KCl of the calomel electrode. It is usually necessary to add a trace of pure gelatine to the solution in E in order to obtain smooth diffusion current curves. The oscillations of the current as the drops form can be greatly reduced by connecting an electrolytic condenser of large capacity, e.g. 2,000 μF, in parallel with the galvanometer.

A large number of phenomena can be studied with the dropping-mercury electrode, but for details of special techniques of polarography reference should be made to the monograph by Kolthoff and
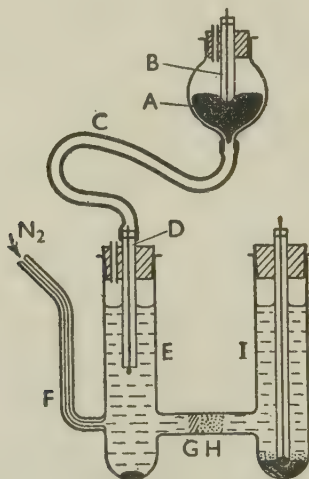
FIG. 11.11. Cell for determination of polarograms with a dropping-mercury electrode.

Lingane.[3] The following polarograms may be determined as examples, using $0.1N$ KCl$+0.1\%$ gelatine as base solution: (a) de-oxygenated base solution, (b) base solution satd. with air, (c) satd. with oxygen, (d) $+0.001M$ Pb(NO$_3$)$_2$, (e) $0.0005M$, $0.001M$ and $0.002M$ CdSO$_4$, (f) $0.001M$ Pb(NO$_3$)$_2+0.001M$ CdSO$_4$, (g) $0.001M$ FeCl$_3$ (gives double "wave"), (h) $0.001M$ saccharin, (i) amperometric titration of 50 ml of $0.01M$ lead nitrate with $0.05M$ potassium dichromate at a fixed potential of -1.0 V with respect to satd. calomel electrode.

BIBLIOGRAPHY 11B: Electrode processes

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ELECTROMOTIVE FORCE OF CELLS

12A. THEORY OF CELLS

Introduction

Voltaic cells play an important part in physical chemistry because they provide a convenient means of measuring directly the "affinity" or *free energy change* accompanying certain reactions. When a voltaic cell is discharged, the free energy of the *cell reaction* becomes available for performing useful work. The *maximum useful work* is obtainable in theory only by discharging the cell infinitely slowly so that its maximum electromotive force (e.m.f.) is exerted. In practice, this means that the open-circuit e.m.f. of the cell must be measured; this can be done by determining the e.m.f. that must be applied in opposition to that of the cell in order that no current shall flow when the circuit is closed—the "Poggendorff compensation method".

If the e.m.f. of a cell (on open circuit) is E volts, the maximum amount of electrical work that could be drawn from the cell is $E \times Q$ volt-coulombs (= joules), where Q is the number of coulombs of electricity obtainable from the cell. It is usual to state thermo-chemical quantities for the number of moles of substances shown in the equation expressing the cell reaction, and this may provide n g equivalents, each of which, by Faraday's Laws, will be accompanied by 1 Faraday ($F = 96,500$ coulombs) of electricity. Therefore the amount of electrical work obtainable from the cell reaction is given by nEF joules. This quantity is equal to the decrease of Gibbs free energy in the reaction ($-\Delta G$). Furthermore, a study of the e.m.f. of the cell at different temperatures provides a value for the entropy change in the reaction (ΔS), since $\partial \Delta G / \partial T = -\Delta S$, and hence the heat of the reaction can also be calculated, using the equation $\Delta G = \Delta H - T \Delta S$. This method of obtaining thermodynamic quantities is far more convenient than the laborious method of thermal data or the method of studying chemical equilibria, but is restricted, of course, to reactions involving an electron transfer. Also, in practice, relatively few satisfactory ("reversible") electrodes are available for employment in cells.

In many applications of voltaic cells the e.m.f. measurements are used to obtain information about the constitution of solutions—for

example, the concentration of hydrogen ions. The relationship between constitution and e.m.f. is of great importance, and may be derived by thermodynamics in various ways; one derivation is given in the section that follows. The theory of electrode potentials was first given in approximate form by Nernst in 1889, who obtained the formula

$$E_M = \text{constant} + \frac{RT}{zF} \log_e C_M$$

for the e.m.f. of a metal electrode (z = valency, C_M = concentration of metal ions), and

$$E_H = \text{constant} + \frac{RT}{F} \log_e \frac{[H^+]}{p_{H_2}^{\frac{1}{2}}}$$

for the e.m.f. of a hydrogen electrode. ([H^+] = concn. of hydrogen ions, p_{H_2} = pressure of hydrogen gas.) The Nernst formulae were used for many years, but, as will be seen below, the exact theory involves thermodynamic *activities* rather than concentrations.

General thermodynamic theory of electrode potentials. Every voltaic cell consists of two *electrodes* or "half-cells" which are connected internally by the electrolyte solution and externally by the leads and potential-measuring instruments. It is a useful convention (though not strictly an essential device) to imagine that each electrode sets up its own potential difference *with respect to the solution*. Although these "single electrode potentials", E_1 and E_2, are not susceptible to measurement separately, their algebraic difference is the measured e.m.f. of the cell, i.e. $E = E_1 - E_2$. E_1 and E_2 may be either positive or negative quantities with respect to the solution, depending on the nature of the electrode. Their e.m.f. may, therefore, either oppose one another (if they are of the same sign) or reinforce (if they are of opposite sign), and the algebraic difference will determine which electrode becomes the positive pole of the cell.

Each electrode can be considered the seat of an electrochemical reaction in which an electron ($\ominus$) passes from the electrode to an ion in the solution, or vice versa, according to the equation $X \rightleftarrows X_{aq}^+ + \ominus$ for cationic electrodes (such as the silver and hydrogen electrodes), or $Y_{aq}^- \rightleftarrows Y + \ominus$ for anionic electrodes (such as the chlorine electrode), or $Z_{aq}^{++} \rightleftarrows Z^{+++} + \ominus$ for oxidation-reduction electrodes. The electrode reaction can be considered to proceed until a certain difference of potential is set up between the metal and the solution (because of the transference of electrons involved). *Suppose the metal attains a potential E_1 volts with respect to that of the solution**. At equilibrium the tendency of the reaction to proceed is exactly balanced by the opposing electrical potential (E_1). In other words, the electrical work *required* to transfer an electron from one phase to the other exactly counterbalances the free energy *released* by the *chemical* process of the cell reaction, the net free energy change being zero. The electrical work for moving one electron through a potential difference

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* American physical chemists use the opposite convention.

E_1 is $E_1 \times$ the electronic charge, or $E_1 \times F$ for 1 g equiv. of electrons. The free energy change produced by converting 1 g equiv. of X into X^+ is $(\mu_{X^+} - \mu_X)$, where μ means the *chemical potential* (partial molar free energy) of the species. The chemical potentials are related to the thermodynamic activities (a) by the equation $\mu = \mu^\circ + RT \log_e a$, where μ° is the chemical potential of the substance in its *standard state*, for which the activity is defined as unity.

If the electrode reaction $X = X^+_{aq} + \ominus$ goes from left to right, one equivalent of *electrons* passes to the electrode, which is at potential E_1, measured on a nominally positive scale of potential. Therefore, the transference of electrons in this direction is accompanied by a release of energy, and consequently the net change of free energy of the system is

$$\Delta G = \mu_{X^+} - \mu_X - E_1 F = 0$$

Hence,

$$E_1 = \left(\frac{\mu^\circ_{X^+} - \mu^\circ_X}{F} \right) + \frac{RT}{F} \cdot \log_e \frac{a_{X^+}}{a}$$

The term $(\mu^\circ_{X^+} - \mu^\circ_X)/F$ is a constant, and clearly equal to the value that E_1 would assume for an electrode in which $a_{X^+} = 1$ and $a_X = 1$, i.e. with the reactant and product in their standard states. This e.m.f. is denoted E°_1, and termed the *standard electrode potential* for the X electrode. Thus, with other concentrations, these electrodes have an e.m.f. given by

$$E_1 = E^\circ_1 + \frac{RT}{F} \cdot \log_e \frac{a_{X^+}}{a_X}$$

Some electrode reactions involve transference of more than one electron; thus, $Cu \rightleftarrows Cu^{++} + 2\ominus$ involves two. In the general case of z electrons, the *general formula for a single electrode potential is*

$$E_x = E^\circ_x + \frac{RT}{zF} \log_e \frac{a_{X^{z+}}}{a_X}$$

Specific examples of the application of this formula to various practical electrodes are given later.

It will be noticed that e.m.f. measurements primarily give information about thermodynamic *activities*; however, these can often be related to the *concentrations* of the substances concerned (see below).

Since single electrode potentials cannot be measured, it is the accepted convention to take the standard hydrogen electrode (see below) as arbitrary zero of e.m.f., and to tabulate other electrode potentials relative to the standard hydrogen electrode. Thus, if an electrode, when coupled with a standard hydrogen electrode gives $+E$ volts, the electrode potential is $+E$; if it reads negative to the hydrogen electrode, the electrode potential is negative.*

Activity coefficients of salts. It has been mentioned above that electrode potentials are dependent upon the thermodynamic *activity* of the ions in solution. In general the activity of any species i

* cf. footnote on p. 240.

differs somewhat from its concentration (say molality, m) by a factor f called the activity coefficient; thus, $a_i = m_i f_i$ and $f_i \to 1$ as $m_i \to O$. Activity coefficients can be measured in a number of independent ways such as from f.p. depressions (p. 113) and, of course, conversely, from e.m.f. of cells. In the case of a non-electrolyte, e.g. alcohol in water, the factor f is unambiguous, but with electrolyte solutions care is needed in defining and applying activity coefficients. The usual treatment is therefore given here briefly.

The chemical potential of a salt is regarded as the sum of the chemical potentials of its constituent ions. Thus, for a uni-univalent (1:1) electrolyte $\mu_{salt} = \mu_+ + \mu_-$. The activity of a salt is therefore the *product* of the activities of its ions, $a_{salt} = a_+ \times a_-$. Since a_{salt} is a quantity that can be measured (for example, from f.p. depression determinations), whereas there is no sound method of splitting it into a_+ and a_-, it is usual to work in terms of the *mean ion activity* $u_\pm$ defined by $a_\pm = \sqrt{a_{salt}}$. Similarly, although individual ions are regarded as having individual activity coefficients, f_+ $(= a_+/m_+)$ and f_- $(= a_-/m_-)$, these are not separately determinable, but a mean value $f_\pm$, defined by $\sqrt{f_+ f_-}$, is obtainable, since $a_{salt} = a_+ a_- = (f_+ m_+)(f_- m_-) = f_\pm^2 m_+ m_- = f_\pm^2 m_\pm^2$, where $m_\pm$ is the mean molality $(= \sqrt{m_+ m_-})$. The formulae for salts of other valence types are analogous although somewhat more complicated.[1] *In the case of electrolytes the activity coefficients generally tabulated are the mean ion activity coefficients, $f_\pm$.* Many experimentally determined activity coefficients are now available.[2] Some values for a number of common electrolytes are given in Table A10 in the Appendix. The values are quoted for 25° C, but they do not change much with temperature.

Estimation of activity coefficients. A theory of the activity coefficients of salts has been given by Debye and Hückel (1923). The theory leads to the following approximate expression for the activity coefficient f of an ion in a *very dilute* electrolyte solution:

$$-\log_{10} f \approx 0{\cdot}5 z^2 \sqrt{\mu}$$

where z is the valency of the ion and μ is the *ionic strength* of the solution, defined by $\mu = \frac{1}{2} \Sigma m_i z_i^2$; the summation is for every type of ion (molality m_i and valency z_i) present in the solution. In the case of a pure 1:1 salt, ionic strength is equal to molality, but not in other cases.

The simple Debye-Hückel formula holds up to about $0{\cdot}01 N$ for 1:1 salts. For higher concentrations more complicated expressions have been derived, but they are of very limited usefulness. The theoretical formulae are not satisfactory for trivalent and polyvalent ions.

It is often necessary to make an estimate of the value of the activity coefficient of an ion, in the absence of experimental values for it. If the ionic strength is less than 0·01 the simple Debye-Hückel formula may be

used.   A more reliable value is obtainable from a formula of Güntelberg [3] namely, for a salt of valence type $z_+ : z_-$, $\log f_\pm = -0.5 z_+ |z_-| \sqrt{\mu}/(1 + \sqrt{\mu})$. This gives a useful representation of the *average* behaviour of salts up to $\mu = 0.1$, and is as good a *guess* as any other.

A still better value can be obtained if it is possible to calculate the empirical constant, β, in the extended Güntelberg equation [4]: namely

$$\log f = -0.5 z_+ |z_-| \sqrt{\mu}/(1 + \sqrt{\mu}) + 2\beta\bar{\nu}$$

where $\bar{\nu}$ is given by $2/\bar{\nu} = 1/\nu_+ + 1/\nu_-$.   (Here ν_+ and ν_- are the concentrations of cation and anion respectively.)   The constant, β, can be calculated provided the activity coefficient of at least one solution of the salt has been determined.   A list of values recommended by Guggenheim [5] is given in Table 12.1.

The Güntelberg-Guggenheim formula can be used for estimating activity coefficients in salt mixtures.

TABLE 12.1

Empirical β constants for calculation of activity coefficients from the Güntelberg-Guggenheim equation *

Electrolyte		Electrolyte	
HCl	0·24	KNO$_3$	−0·21
NaCl	0·12	Na$_2$SO$_4$	−0·39
KCl	0·07	K$_2$SO$_4$	0·00
LiCl	0·20	MgSO$_4$	0·00
TlCl	0·35	CuSO$_4$	−1·5
KClO$_4$	−0·44	La(NO$_3$)$_3$	2·25
NaNO$_3$	0·00	CaCl$_2$	0·75

* Guggenheim, *Phil. Mag.*, 1935, **19**, 588; 1936, **22**, 322.

Types of electrode and cell.   Although in principle any reaction involving transference of electrons is capable of providing an electrode, comparatively few reliable electrode systems are available. To be satisfactory an electrode must be *electrochemically reversible*; that is to say, if an external potential *slightly* greater than that of the electrode is applied in one direction the electrode reaction must proceed quantitatively from left to right and if the potential is reversed the reaction must be quantitatively reversed.   Some possible electrodes are imperfectly reversible because side reactions occur. The following list includes most of the more satisfactory practical electrodes.

(a) *Metal electrodes.*   A metal dipping into a solution of one of its salts.   The electrode reaction is $M \rightleftarrows M^{z+} + z \ominus$ and the electrode potential $E_M = E_M^\circ + \dfrac{RT}{zF} \log \dfrac{a_{M^{z+}}}{a_M}$.   If the electrode consists of pure metal M, $a_M = 1$.   (Examples: silver, mercury, lead, zinc, cadmium, copper.)

In *alloy* electrodes, the metal M is in solution (solid or liquid) at an activity a_M less than unity. (Examples: cadmium amalgam—used in Weston cells, alkali metal amalgams.)

A modified type of metal electrode is one in which the concentration of metal ion in solution is controlled by keeping the solution saturated with a sparingly soluble salt of the metal, M^+A^-. (Examples: the calomel electrode (p. 251), the silver–silver chloride electrode (p. 259).) By the common ion effect, the concentration (or, rather, activity) of the metal ion is inversely proportional to the concentration (activity) of the anion of the salt. Such electrodes are therefore effectively reversible with respect to the anion, their potential being given by an expression of the form

$$E = E° + \frac{RT}{zF} \log \frac{1}{a_{A^-}}$$ where A^- is the relevant anion.

(b) *Gas electrodes.* The reaction $H_2 \rightleftarrows 2H^+ + 2\ominus$ is catalyzed by the surface of platinum, palladium, or gold, the metal acting as acceptor of the electrons and therefore assuming a potential given by

$$E_H = E_H° + \frac{RT}{2F} \log_e \frac{a_{H^+}^2}{p_{H_2}} = E_H° + \frac{RT}{F} \log_e \frac{a_{H^+}}{p_{H_2}^{\frac{1}{2}}}$$

As mentioned above, it is the recognized convention to take the standard hydrogen electrode (having $p_{H_2} = 1$ atm, $a_{H^+} = 1$) as the arbitrary zero of electrode potential. Thus, on this convention, $E_H° = 0$, and

$$E_H = \frac{RT}{F} \log_e \frac{a_{H^+}}{p_{H_2}^{\frac{1}{2}}}.$$ In practice, other gas electrodes (chlorine, oxygen) are less satisfactory than the hydrogen electrode.

(c) *Oxidation-reduction* ("*redox*") *electrodes.* Chemically unreactive metals such as platinum can also serve as electron acceptors (and therefore potential-indicators) for reactions involving solutes in two states of oxidation. For example, if the electrode reaction is $X^{n+} \rightleftarrows X^{(n+z)+} + z\ominus$ the electrode potential is given by $E_r = E_r° + \frac{RT}{zF} \log_e \frac{a_X^{(n+z)+}}{a_X^{n+}}.$ Examples:

$$Fe^{++} \rightleftarrows Fe^{+++} + \ominus; \quad Sn^{++} \rightleftarrows Sn^{++++} + 2\ominus; \quad Ce^{+++} \rightleftarrows Ce^{++++} + \ominus;$$
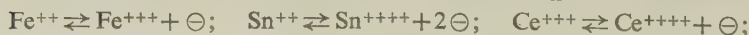
quinone–hydroquinone (see below)).

(d) *Membrane electrodes.* If a membrane is selectively permeable to one kind of ion only, it can be used to compare the activities of the ion in two solutions placed on opposite sides of the membrane by means of measurements of the "membrane potential". The only important example is the *glass electrode*, which is selectively permeable to hydrogen ions and is therefore used for comparing the pH values of solutions (p. 266). The theoretical membrane potential is given by

$$E = \frac{RT}{F} \log_e \frac{a_{H_1^+}}{a_{H_2^+}}$$

Cells. A cell may be constructed by joining the electrolytes of any two half-cells. Clearly two types of cell may be distinguished: (a) those in which the two half-cells employ the same electrolyte solution, but, of course, have different electrodes, e.g. $H_2(Pt) | H^+$

(in N HCl), with $Hg \mid Hg_2Cl_2$ in N HCl, and (b) those in which the two half-cells contain *different* electrolyte solutions, which therefore have to be connected together at a *liquid junction*, e.g. the cell $H_2(Pt) \mid H^+$ (in $N\,H_2SO_4)\|N$ KCl, $Hg_2Cl_2 \mid Hg$. The double vertical line denotes the liquid junction.

Liquid junction potentials. Whereas the e.m.f. of cells "without junction" (sometimes termed "without transport") is unambiguously given by the algebraic difference between the separate electrode potentials, the presence of a liquid junction may introduce an additional source of potential known as the *liquid junction potential* E_j (or "diffusion potential", since it arises from the unequal rates of diffusion of the ions in the electrolytes at the junction). The net e.m.f. of the cell is then $E = E_1 - E_2 + E_j$.

The magnitude of liquid junction potentials can be calculated in certain simple cases. For example, at a junction between two solutions consisting of different concentrations of the same uni-univalent salt, it is given by

$$E_j = \frac{RT}{F} \cdot \frac{(u-v)}{(u+v)} \log_e \frac{a_1}{a_2}$$

where u and v are the *mobilities* of the cation and anion respectively, and a_1 and a_2 are the activities of the salt in the two solutions. In many cases, however—notably when the two solutions contain different electrolytes—the liquid junction potential cannot be calculated. If it were neglected it might lead to unknown errors in results. The usual practice is to reduce, "swamp" or "eliminate" the liquid junction potential by joining the solution via a "salt bridge" consisting of a concentrated solution of a salt having $u \approx v$, usually KCl or KNO_3. Since the theory indicates that E_j arises through unequal diffusion of anion and cation, the presence of a high concentration of ions of equal mobility is thought to reduce the junction potential to a negligible value. Normally E_j is only a few millivolts, but in the important case of junctions involving *acids* it may be much more, because H^+ has a much higher mobility than other ions. The degree of success attending the use of salt bridges with rather concentrated acid solutions is not known, and this uncertainty limits the accuracy and significance of pH measurements (p. 266).

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[1] See Harned and Owen, *op. cit.*

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12B. PRACTICAL METHODS

Measurement of the e.m.f. of a cell: outline of the method.   The e.m.f. of a cell is generally measured by means of a potentiometer circuit.   A steady external source of potential is adjusted until no current flows when it is connected in opposition to the cell.   The basic principle of the potentiometer can be understood from Fig. 12.1. A cell of large capacity, B, discharges through a calibrated resistance PQ which carries a movable contact, X.   It follows from Ohm's Law that, provided no current passes through the contact X, there is a uniform potential gradient (in volts per ohm) through PQ, and the

FIG. 12.1. Basic principle of the potentiometer.

potential difference across any section of it is proportional to the resistance of that section.   The cell C_1 is now connected as shown, with like poles of B and C_1 connected to P. G is a sensitive galvanometer.   When the key K is momentarily closed, current passes in one direction or another—as indicated by G—unless the contact X is at the precise point on PQ at which the potential equals that of C_1.   Provided the e.m.f. of B exceeds that of C_1 a balance point can be found by moving X until on closing K no current passes.   The potential drop along PX is then equal to the e.m.f. of the cell.

However, the e.m.f. of the working cell, B, is not accurately known, and therefore use is made of a reference or "standard" cell, C_2, of known e.m.f.   Such a cell can be preserved without change of e.m.f. because it is not called upon to provide more than an infinitesmal current.   A new balance point, X' is now found for C_2 exactly as for C_1, and hence,

$$\frac{\text{e.m.f. of } C_1}{\text{e.m.f. of } C_2} = \frac{\text{Resistance } PX}{\text{Resistance } \overline{PX'}}$$

Formerly the potentiometer resistance PQ consisted of a metre of resistance wire along which a sliding metal contact could be moved; relative resistance PX and PX' were then read from the *lengths* PX and PX'.   The metre wire has now been superseded by the more

accurate and convenient direct-reading potentiometers described below.* The principle, however, remains the same.

The potentiometer. Fig. 12.2 shows a typical laboratory potentiometer suitable for the measurement of the e.m.f. of cells. The methods of operation can be best understood by consideration of the circuit diagram (Fig. 12.3).

The metre wire of the simple potentiometer (Fig. 12.1) is replaced by a series of 18 2-ohm standard resistors, R_1, and a circular 2-ohm slide-wire, R_2, graduated at every 0·5 mV. The potential across $R_1 + R_2$ is first adjusted to be exactly 1·9 V. This is effected by means of the auxiliary standardization circuit (shown by the broken
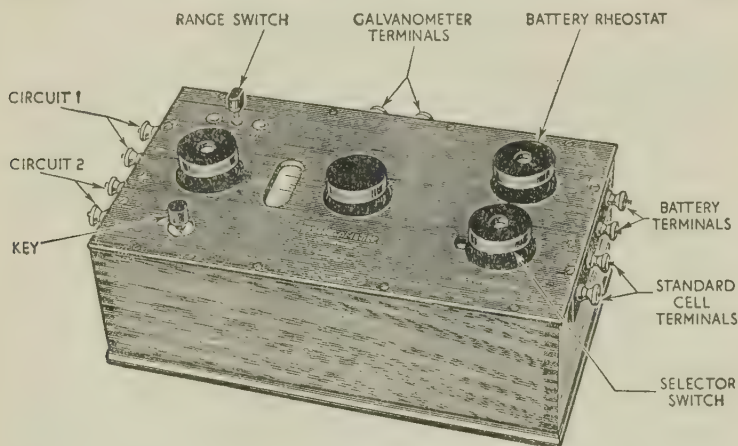
Fig. 12.2. General purpose laboratory potentiometer.
(Courtesy Messrs. H. Tinsley and Co., Ltd., London.)

lines in Fig. 12.3), by means of which the standard cell, C, can be balanced across the ratio arms, R_3 and R_4. The rheostat R_5 is adjusted until, on closing the key S_3, no deflection is produced on the galvanometer. When this adjustment has been made, the potential across R_3 must equal that of the standard cell, 1·0186 V, and the potential across $R_1 + R_2$ is then known to be 1·9 V since $R_3 : (R_3 + R_4) = 1·0186 : 1·900$. In making a measurement of the e.m.f. of an external source, the selector switch S_2 is put into the position shown and a balance for no deflection is obtained by adjusting R_1 and R_2. The e.m.f. of the external source is then given by the sum of the dial readings on R_1 and R_2.

* "From the pedagogical point of view they have the disadvantage of indicating e.m.f. values without forcing the student to understand the principle"— Kolthoff and Laitinen, 1941.

The range switch S_1 is provided to allow the instrument to measure smaller e.m.f. values with corresponding accuracy. Whereas the operation of standardizing the instrument always sets a potential of 1·9 V between the points A and B, the network of resistors R_5, R_6, R_7, and R_8 is prearranged to produce, 1·9, 0·19, or 0·019 V across $R_1 + R_2$ according to the setting of S_1. (The network is employed so that the total resistance shunted across AB is the same for every position of S_1; the standardization is therefore unaltered.) The

FIG. 12.3. Circuit diagram of laboratory potentiometer.

greater sensitivity is useful in studying the temperature coefficient of e.m.f. of cells or the small e.m.f. produced by thermocouples (pp. 41-2).

Several other potentiometers of slightly different design are also available, but the only one that will be mentioned here is the very convenient portable type such as that shown in Fig. 12.4 in which the standard cell, galvanometer, and battery are all housed in the same case. The principle of operation is similar to that of the instrument already described. Some simpler methods of potentiometry, applicable when lower accuracy is permissible, are described later

(pp. 281–4). Certain pH meters (p. 274) are also adaptable for measuring e.m.f. of cells.

The working cell. The theory of the potentiometer circuit depends on the assumption that a steady source of current is available which will not alter between the operation of standardizing the instrument and that of balancing the cell on test. In practice, this requirement is most satisfactorily met by a single cell lead accumulator of capacity not less than 40 amp-hours. It is advisable to reserve a number of accumulators specifically for potentiometry.
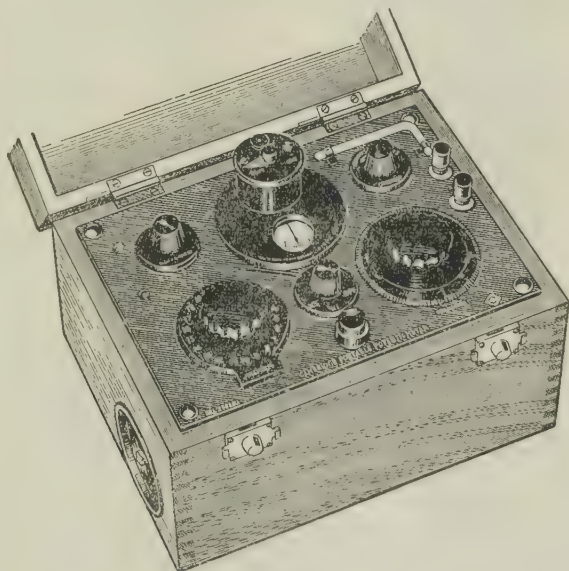
Fig. 12.4. Portable, self-contained, potentiometer.
(Courtesy Cambridge Instrument Co., Ltd., London).

They should be kept well charged (2·1–1·9 volts) and never subjected to heavy discharge. On the other hand, a freshly-charged cell is less satisfactory than one that has stood for a day after charging. The cell should be connected to the potentiometer about 10 minutes before final readings are required, as this makes for steadiness. Portable potentiometers generally have dry cells.

The galvanometer. The most satisfactory instrument for indicating the balance point in accurate potentiometry is the self-contained reflecting galvanometer unit such as that illustrated in Fig. 12.5. Although many other types of galvanometer are, of course, serviceable, it is a great convenience to have ample sensitivity available for the final balance point, and yet be able to make the preliminary

adjustments with a much reduced sensitivity which is instantly obtainable by rotating the contact knob of the adjustable shunt. The use of a low sensitivity at the beginning not only protects the galvanometer from damage, but also makes it easier to see whether the adjustments of potential are being made in the right direction. Illumination for the spot of light is obtained from a 4-volt accumulator or a small mains transformer.   The moving-coil galvanometers employed nowadays have a short, taut suspension and therefore need no levelling and quickly come to rest.   A sensitivity as high as 100
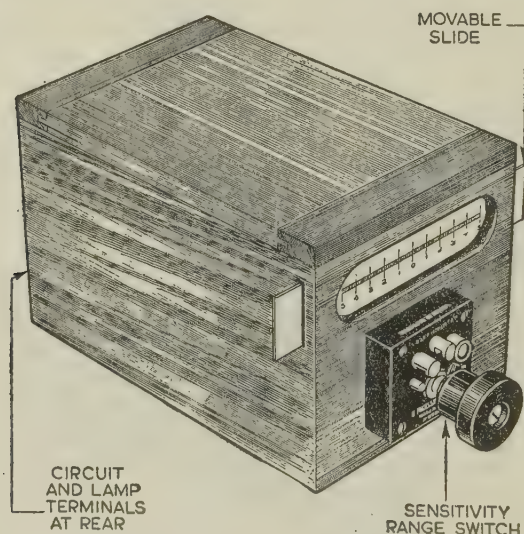
Fig. 12.5. Robust "spot" galvanometer with sensitivity switch.
(Courtesy Messrs. H. Tinsley and Co., Ltd., London.)

mm per microamp is desirable for accurate work, especially with cells containing very dilute electrolytes.

With cells having extremely high resistance, notably the glass electrode, it is necessary to employ a special valve circuit to detect the point of balance (p. 273).

The standard cell.   Various cells have from time to time been recommended as standards of e.m.f. but the most convenient and the one now most generally employed is the Weston standard cell [1] (Fig. 12.6).   This possesses the advantages not only of being easily reproduced, but also of having a small temperature coefficient of e.m.f.   In this cell, mercury forms the positive pole and a cadmium amalgam containing 12·5% of cadmium, the negative pole.   The electrolyte is a saturated solution of hydrated cadmium sulphate

$3CdSO_4.8H_2O$. The e.m.f. of the original, neutral, standard cells was defined as 1·01830 international volts. Commercial manufacturers of cells generally make the so-called "acid cells" which are more stable.[2] These usually have an e.m.f. of 1·01859 absolute
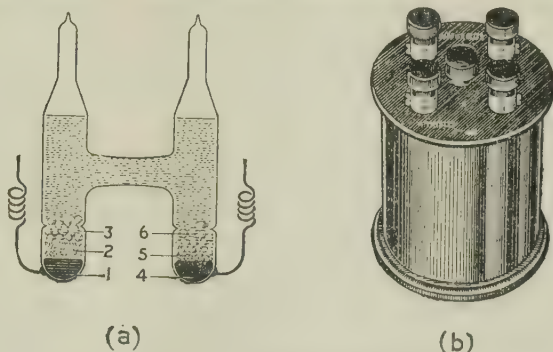
FIG. 12.6. Weston standard cell.
(a) Construction of cell. (b) Pair of mounted cells.

1. Mercury.   2. Paste of cadmium sulphate and mercurous sulphate.   3, 6. Large crystals of cadmium sulphate.   4. Cadmium amalgam.   5. Small crystals of cadmium sulphate.

(Courtesy Messrs. H. Tinsley and Co., Ltd., London.)

volts at 20° C and a temperature coefficient of −40 microvolts per 1° rise of temperature. Standard cells must, of course, be kept upright, and must never be allowed to pass more than a few microamperes of current. Consequently, the potentiometer key should be depressed only momentarily when the balance point is being found.

Measurement of electrode potentials. In order to measure the conventional potential between an electrode and a solution, it is necessary to have another electrode and solution, the potential difference between which is known. As a convenient sub-standard electrode the normal calomel electrode is generally used, because the standard hydrogen electrode is not easy to set up (p. 260). The calomel electrode consists of mercury in contact with a solution of potassium chloride saturated with mercurous chloride. As a vessel to contain the mercury and the solution, one

FIG. 12.7. Convenient form of calomel electrode.

may use a small, wide-mouthed bottle but one of the most convenient forms of vessel is shown in Fig. 12.7.

Preparation of the calomel electrode. First prepare the normal solution of potassium chloride, using pure recrystallized potassium

chloride (dried) for the purpose. In the bottom of the electrode vessel, previously thoroughly dried or washed out with the solution of potassium chloride, place a small quantity (1–2 ml) of pure mercury, and over this a *thin* layer of calomel paste prepared by rubbing together in a mortar calomel and mercury with some of the solution of potassium chloride. It is then washed two or three times with a quantity of the potassium chloride solution, the mixture being allowed each time to stand until the calomel has settled, and the solution then decanted off.

Having placed the mercury and the calomel paste in the tube insert a rubber stopper or paraffined cork carrying the glass tube *C* with platinum wire, which must be immersed in the mercury at the bottom of the tube. The vessel is then filled with the solution of potassium chloride by sucking in the solution through the bent side tube *A*, and then closing the rubber tube on *B* with a clip.

Since the usual convention is to take the standard hydrogen electrode rather than the calomel as the zero of electrode potential, it is necessary to know the electrode potential of the calomel half-cell on the hydrogen scale. This has been determined from cells consisting of a calomel electrode coupled with a hydrogen electrode. The following values [3] may be adopted for calomel electrodes containing three different concentrations of KCl. (Since earlier workers gave somewhat different values, it is desirable to state the value which is adopted for the e.m.f. of the calomel electrode when reporting measurements in which calomel half-cells have been used.)

$$0.1N \text{ KCl calomel electrode}: \; +0.336 - 0.00006(t-25)$$
$$N \text{ KCl calomel electrode}: \; +0.283 - 0.0002 \; (t-25)$$
$$\text{satd. KCl calomel electrode}: \; +0.244 - 0.0007 \; (t-25)$$

Other sub-standard reference electrodes sometimes used are the silver–silver chloride electrode (p. 259), the quinhydrone—"standard acid"—cell (p. 271) and mercury–mercuric oxide cell.[4]

It is relevant to mention here that discrepancies in the literature between values reported for these electrode potentials arise largely from the uncertainty of liquid junction potentials in the different cells used by different workers.

Construction of cells: the salt bridge. When both electrodes of a cell have the same electrolyte solution it is immaterial how the halves are connected; the two electrodes may be either in the same vessel or in separate compartments connected by a tube containing the electrolyte. With all other cells, however, a "liquid junction" is inevitably present at some point, and the usual practice is to interpose a "salt bridge" between the two solutions to minimize the liquid junction potential. The salt bridge usually consists of a

saturated solution of KCl, but if chloride is objectionable, as with silver salts, ammonium nitrate or potassium nitrate is used.

Since the form of the junction can affect the junction potential, it is desirable to have a symmetrical plane of contact between the solutions, with diffusion as the only cause of mixing. It is usual to connect two half-cells, containing relatively dilute solutions, by dipping the connecting tubes of both electrode vessels into a small beaker containing the concentrated salt-bridge solution, as in Fig. 12.8 (a).

When this arrangement is not applicable because the electrode vessel has to be open to the air and syphoning would take place (as in potentiometric titrations), a *solidified* link consisting of a conducting jelly is used to make electrical contact, as in Fig. 12.8 (b). A suitable jelly is prepared by dissolving about 3 g of KCl
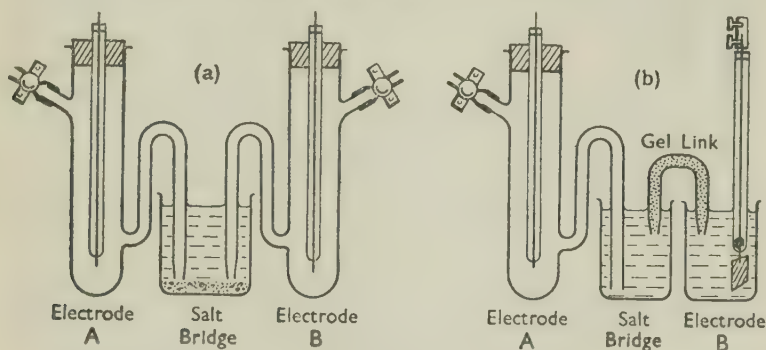
FIG. 12.8. Methods of joining two electrodes to form a cell.

and 0·3 g of agar powder in 10 ml of water; the constituents are heated in a small beaker on a steam-bath, and when a clear solution is obtained it is sucked or poured while hot into U-tubes made from narrow quill tubing. The mixture sets to a gel on cooling. The tubes can be stood in saturated KCl solution until required. After use they must be renewed if there is any possibility of contamination having occurred. Agar gels with KNO_3 or NH_4NO_3 in place of KCl can be used where necessary.

BIBLIOGRAPHY 12B: Practical methods

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2 See Vigoreaux and Webb, *Principles of Electrical and Magnetic Measurements*, 1946 (Blackie, London).
3 Hitchcock and Taylor, *J. Amer. Chem. Soc.*, 1937, **59**, 1812; MacInnes, Belcher, and Shedlovsky, *ibid.*, 1938, **60**, 1094.
4 Fried, *Z. physik. Chem.*, 1926, **123**, 406; Harned and Cook, *J. Amer. Chem. Soc.*, 1937, **59**, 496.

12C. METAL ELECTRODES

The silver electrode. The $Ag|Ag^+$ electrode is one of the most convenient and reproducible metal electrodes, because silver is readily obtainable in a state of high purity, is little affected by oxygen and, being soft, is not much influenced by strain and other physical factors such as grain size.

A simply constructed silver electrode unit is shown in Fig. 12.9 in which a and a' are duplicate rods of pure silver inserted through the rubber bung b. The rods are first cleaned for a few moments in dilute nitric acid, and then electroplated in a 1% solution of $AgNO_3$ in 90% methanol–water, using as anode a platinum wire mounted in a glass tube. A 2-volt accumulator provides sufficient current to produce a thin coating of small crystals of silver on the wires in the course of two or three hours. The electrodes are rinsed with the solution that is to be used in the cell, and are then mounted in position in the vessel containing the solution. A check on the quality of the electrodes is obtained by comparing the e.m.f. of the duplicates. The terminals on the two silver wires are connected to the potentiometer and the e.m.f. determined. Clearly, if the duplicates do not give almost exactly the same e.m.f. (so that when in opposition they give zero volts) they cannot be considered satisfactory and must be electroplated again.
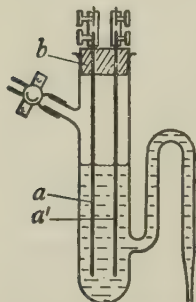
FIG. 12.9. Construction of duplicate silver electrode unit.

EXPERIMENT

Determine the standard electrode potential of the silver electrode at room temperature, and examine the applicability of the theory of concentration cells.

Procedure. Prepare *two N* calomel electrodes (p. 251) and *two* silver electrode units (Fig. 12.9). Fill one of the latter with exactly $N/10$ and the other with $N/100$ silver nitrate solution. Arrange the two calomel vessels and two silver electrode vessels around a small beaker containing saturated potassium nitrate solution into which the tips of the electrode vessels should just dip.

Connect up a potentiometer circuit, with accumulator, and after 10 minutes standardize the potentiometer as described (p. 247). In all work with a potentiometer the *key should be closed only momentarily* to avoid polarizing the standard cell or the cell on test.

When the potentiometer has been standardized, the e.m.f. of the following electrode pairs should be determined to an accuracy of 0·1

mV. Only the connecting leads need be moved to obtain all the combinations of half-cells. *The polarity of every cell should be noted.*

(a) Calomel against calomel.

(b) Ag | $N/10$ AgNO$_3$ duplicate electrodes against one another.

(c) Ag | $N/100$ AgNO$_3$ duplicate electrodes against one another.

Any of these duplicates that differ by more than, say, 1 mV should be dismantled and prepared afresh. If the duplicates agree, then the following cells should be measured:

(d) Ag | $N/10$ AgNO$_3$ ‖ satd. KNO$_3$ ‖ $N/10$ KCl, Hg$_2$Cl$_2$ | Hg

(e) Ag | $N/100$ AgNO$_3$ ‖ satd. KNO$_3$ ‖ $N/10$ KCl, Hg$_2$Cl$_2$ | Hg

(f) Ag | $N/10$ AgNO$_3$ ‖ satd. KNO$_3$ ‖ $N/100$ AgNO$_3$ | Ag

The effect of dispensing with the salt bridge can be tried by replacing the potassium nitrate in the beaker by $N/10$ AgNO$_3$ into which the two silver electrode vessels are dipped (the liquid in the connecting
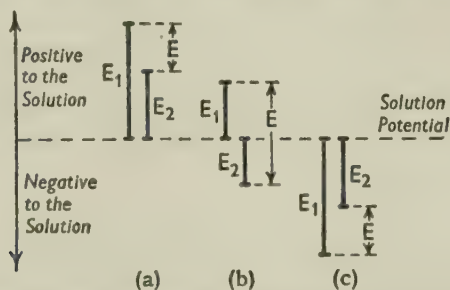
Fig. 12.10. Diagrammatic representation of e.m.f. of a cell as the algebraic difference between separate electrode potentials.

tubes having first been flushed clear of any KNO$_3$ which may have diffused in). Thus the e.m.f. of the following cell can be obtained.

(g) Ag | $N/10$ AgNO$_3$ ‖ $N/100$ AgNO$_3$ | Ag

The temperature of the cells should be recorded at the time of measuring their e.m.f.

The first step is to decide the *sign* and value of the separate electrode potentials. A diagram such as that in Fig. 12.10 helps to avoid confusion. The single electrode potentials are represented by vertical lines which begin at a level corresponding to the potential of the solution, supposed at zero (earth) potential; this is also the potential of the standard hydrogen electrode by convention. Electrodes which are positive to the hydrogen electrode rise above the zero level, and those which are negative fall below, the length of the lines being proportional to the e.m.f. of the electrodes. The measured e.m.f. of the cell is the difference of potential, E, between the outer ends of the lines for the pair of electrodes. The positive

pole of the cell is clearly the electrode rising the higher on the diagram.

Three cases are possible: (a) both electrodes positive with respect to the hydrogen electrode, (b) one positive, one negative, (c) both negative. Since one of the half-cells will generally be a reference electrode such as a calomel half-cell, its line on the diagram will be known in sign and magnitude. The potential of the normal calomel electrode, for example, is 0·281 V (25° C) *positive*. If the other electrode is positive with respect to the calomel electrode, it must have a potential more positive than 0·281 V as in case (a) ($E_1 > E_2$). If the other electrode is negative with respect to calomel, the cell could be the opposite instance of case (a), the calomel being the higher, in which case E ($= E_1 - E_2$) will be less than 0·281 V, or of case (b), if E is more than 0·281 V.

In short, consideration of the polarity of the cell, its e.m.f. and the sign and e.m.f. of the reference electrode will always give a check on the sign of the unknown electrode potential. The correct result can, of course, be obtained by rigid application of the algebraic difference formula. Thus, if the electrodes are arbitrarily labelled a and b, and E_{ab} is the potential, including the sign, of a with respect to b, and E_{as} and E_{bs} are the potentials of a and b with respect to the solution, then

$$E_{ab} = E_{as} - E_{bs}$$

Any term in this formula can have a positive or negative value.

In the present experiment, the e.m.f. of the calomel electrode at the temperature of the experiment should be calculated from the formula on p. 252, and hence the e.m.f. of the silver electrode in cell (d) can be calculated (E_{Ag}).

The e.m.f. of a silver electrode is given by

$$E_{Ag} = E_{Ag}^{\circ} + \frac{RT}{F} \log_e a_{Ag^+} = E_{Ag}^{\circ} + \frac{2 \cdot 303 RT}{F} \log_{10} a_{Ag^+}$$

where E_{Ag}° is the standard electrode potential of the $Ag | NO_3^-$ electrode, and a_{Ag^+} is the activity of silver ions in the solution.

The value of the numerical factor, 2·303RT/F, which occurs in all calculations on cells, is given for various temperatures in the table on page 257. (For intermediate temperatures it may be calculated from the approximate formula $0·05420 + 0·0001985t(° C)$.)

In order to obtain E_{Ag}° one needs to know a_{Ag^+}; this is taken to be equal to the mean ion activity of the silver and nitrate ions in the solution, and is therefore obtained by multiplying the molality of the $AgNO_3$ by the appropriate activity coefficient, values of which are given in Table A10. Thus, for $N/10\ AgNO_3$, $a_{Ag^+} = 0·1 \times 0·733$.

Value of the factor 2·303 RT/F in absolute volts* for different temperatures

$t°$ C		$t°$ C	
0	0·05420	22	0·05857
10	0·05619	24	0·05897
12	0·05658	25	0·05916
14	0·05698	26	0·05936
16	0·05738	28	0·05976
18	0·05777	30	0·06016
20	0·05817	40	0·06214

* The absolute volt replaced the old international volt in 1948 (1 int. volt = 1·00033 abs. volt).

Thus, a value for $E°_{Ag}$, the standard electrode potential of the silver electrode can be obtained from cell (d). Another value results similarly from cell (e).

The e.m.f. of cell (f) should be exactly equal, of course, to the difference of (d) and (e), and should be given by the formula for a concentration cell without liquid junction potential ("concentration cell without transport"), namely:

$$E = \frac{RT}{F} \log_e (a_{Ag^+})_1/(a_{Ag^+})_2$$

Cell (g) differs from cell (f) in having a direct liquid junction between $N/10$ $AgNO_3$ and $N/100$ $AgNO_3$, and therefore the difference between their e.m.f. values gives an indication of the liquid junction potential E_j (assuming that in (f) E_j is entirely eliminated by the KNO_3 salt bridge). The experimental value of E_j may be compared with that predicted by the theoretical equation of Henderson which, for $AgNO_3$ solutions, gives

$$E_j = (2t_{NO_3^-} - 1) . \frac{RT}{F} \log_e (a_{Ag^+})_1/(a_{Ag^+})_2$$

where $t_{NO_3^-}$ is the *transport number* of the Ag^+ ion, and may be taken as 0·53. The total e.m.f. of cell (g) should therefore be given by

$$2t_{NO_3^-} . \frac{RT}{F} \log_e (a_{Ag^+})_1/(a_{Ag^+})_2$$

Experiments with other metal electrodes. Similar experiments may be performed with electrodes of cadmium, copper, lead, mercury, thallium, tin or zinc in $M/100$ and $M/10$ solutions of their salts. The metals should be as pure as possible. Cadmium and zinc electrodes may be amalgamated in order to improve their stability. This is done by placing them in dilute sulphuric acid and rubbing mercury over them with a mop of cotton-wool. Copper electrodes may be scraped, cleaned in dilute nitric acid,

and electroplated with copper from a solution containing 15 g $CuSO_4$, 5 g H_2SO_4, 5 g ethanol, 100 g water, using a pure Cu anode and passing a current of only 5 mA per sq. cm.

Results. Experimental results for standard electrode potentials should be compared with the following values.[1]

Metal electrode	Ag	Hg	Tl	Cu	Zn	Cd	Sn	Pb
Standard potential at 25° C (volts)	0·799	0·798	−0·335	0·34	−0·763	−0·402	−0·140	−0·126

Applications of metal electrodes.

1. *Determination of activity coefficients.* It is an obvious extension of the previous work to use a metal electrode to determine the activity of metal ions in other solutions. Either the standard electrode potential may be taken as known, or a solution of a salt of the metal of known activity may be used as one side of a concentration cell similar to cell (f) above.

EXPERIMENT

Determine the activity coefficient of a solution of a silver salt, e.g. silver acetate up to N/20, or silver fluoride up to N. Alternatively, the effect of KNO_3 (up to N) on N/100 $AgNO_3$ may be studied.

Procedure. Set up pairs of silver electrodes in duplicate as described previously, and measure the e.m.f. of appropriate concentration cells, taking $N/10$ $AgNO_3$ as a solution of known activity and using satd. KNO_3 as salt bridge.

Compare the results with the predictions of the Debye-Hückel theory and the Güntelberg-Guggenheim equation (pp. 242–3).

2. *Solubility of sparingly soluble salts.* When a salt M^+X^- is sparingly soluble it exhibits the "common ion effect", the amount of M^+ ion in solution being related to the concentration of X^- ion by the solubility product, $K_s = [M^+][X^-]$ or, strictly, $K_s = a_{M^+}.a_{X^-}$. K_s can be found by measuring $a_M{}^+$ with an electrode of M, in a solution of definite a_{X^-} saturated with M^+X^-. In the ordinary saturated solution of M^+X^- in pure water $[M^+] = [X^-]$ and activity coefficients may be taken as unity if the solution is very dilute. Hence, the solubility $= \sqrt{K_s}$.

EXPERIMENT

Determine the solubility of silver chloride in water.
    Set up the cell

$$Ag \mid AgCl, 0·01 \ N \ KCl \mid satd. \ KNO_3 \mid 0·01 \ N \ AgNO_3 \mid Ag.$$

The left hand electrolyte is obtained by adding one drop of silver

nitrate solution to $0.01N$ KCl.   Determine the e.m.f. as before and note the temperature.

Calculation.   Treat the cell as a concentration cell without liquid junction.   Take the activity of Ag^+ in $0.01N$ $AgNO_3$ as 0.01×0.892 and hence calculate a_{Ag^+} in $0.01N$ KCl.   Take the activity of chloride ion in this solution as 0.01×0.902, and hence calculate K_s $(= a_{Ag^+} \times a_{Cl^-})$ and the solubility in moles/litre $(= \sqrt{K_s})$ and finally in g/litre.   The value [2] is about 1.9×10^{-3} g/litre at $25°$.

3. *Anion-reversible electrodes.*   Given the result of the preceding experiment, one can employ an electrode consisting of $Ag + AgCl$ to determine chloride ion activities, since the e.m.f. of the electrode is given by $E = E_{Ag}° + (RT/F) \log_e a_{Ag^+} = E_{Ag}° + (RT/F) \log_e (K_s/a_{Cl^-})$ $= E_{Ag/AgCl}° - (RT/F) \log_e a_{Cl^-})$.   Here $E_{Ag/AgCl}°$ is the standard electrode potential of the composite $Ag/AgCl$ electrode, which is readily calculable from the above results.

The silver–silver chloride electrode is often used as a reference half-cell since it is reproducible and stable, and can be inserted into cells containing chlorides without introducing liquid junctions.   The standard e.m.f. is given [3] by

$$E_{Ag/AgCl} = 0.222_4 - 0.0006 \, (t - 25)$$

If used as a reference electrode in place of a calomel, the electrode may be placed in $0.1N$ KCl $(a_{Cl^-} = 0.1 \times 0.771)$.   It is usual to ensure that the solution in immediate contact with the silver surface is properly saturated by providing a porous coating of AgCl on the Ag, for example, by electrolyzing a solution of $0.1N$ HCl at very low current density for half an hour using an ordinary silver electrode (p. 254) as anode.[4]

4. *Equilibrium constants of complex ions.*   This application is an obvious extension of the first.   For example, if the activity of silver in a very dilute solution containing a known amount of ammonia is measured, the extent to which the complex ion $Ag(NH_3)_2^+$ is formed can be estimated.

EXPERIMENT

Determine the e.m.f. of the following cell:

$Ag \,|\, 0.025N$ $AgNO_3$ in N NH_3 solution $\|$ satd. soln. of $KNO_3 \,\|$ $0.01N$ $AgNO_3 \,|\, Ag$.

Calculation.   The reaction is $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$ and hence the thermodynamic equilibrium constant is given by

$$K = \frac{a_{Ag^+} \cdot a_{NH_3}^2}{a_{Ag(NH_3)_2^+}}$$

The e.m.f. determination gives a_{Ag^+} directly.   The activity coefficient for univalent ions in a solution of ionic strength 0.025 may be estimated by comparison with silver nitrate as about 0.9.   Hence $[Ag^+]$ can be calculated, and then $[Ag(NH_3)_2^+]$ and $[NH_3]$. $a_{(AgNH_3)_2^+}$ can be taken as

$0.9 \times [Ag(NH_3)_2{}^+]$ and a_{NH_3} as $[NH_3]$, since this is non-ionic. Thus K can be calculated.

5. *Analytical applications—potentiometric titrations.* See section 12G (p. 280).

BIBLIOGRAPHY 12C: Metal electrodes

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2 Brown and MacInnes, *J. Amer. Chem. Soc.*, 1935, **57**, 4459.
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12D. THE HYDROGEN ELECTRODE

(For theory, see p. 244; applications to pH, pp. 266 *et seq.*)

Preparation of the electrodes. The metallic part of the electrode consists of a small rectangle of platinum foil welded to a piece of platinum wire which is then sealed into a glass tube (Fig. 12.11.) Connection is made by a drop of mercury inside the tube into which a copper lead is dipped. Alternatively, the copper lead can be "soldered" to the platinum inside the tube by means of a small piece of Wood's metal (m.p. 65·5°). It is important that the platinum-glass seal should be sound, and free from cracks.
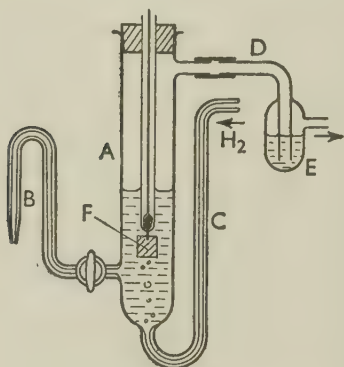
FIG. 12.11. Hydrogen electrode vessel.

The platinum electrode must be platinized before it will function reversibly. The electrode is first cleaned in chromic acid and then well washed with water and finally electroplated in a solution containing about 1 per cent of platinic chloride, using another platinum foil electrode as anode. *Only a very thin, translucent coating of platinum black is wanted.* After the electrolysis, the electrode is washed and then made the cathode in dilute sulphuric acid in order to remove occluded chlorine by the stream of electrolytically-generated hydrogen. After another washing, the electrode is ready for use. It will normally remain active for days if kept under water and protected from "poisoning" (see below).

The electrode vessel. Since the electrolyte has to be saturated with hydrogen and protected from oxygen, it must be contained in an enclosed vessel through which a stream of hydrogen can be passed, and there must be provision for connecting the electrolyte to the other half-cell. A suitable form of apparatus is shown in Fig. 12.11.

The tube, *A*, and connecting arm, *B*, contain the solution.   A stream of hydrogen passes in through the tube *C*, and out via *D* and the small bubbler, *E*, which contains water and serves to keep back air. It is best to have the electrode tube in a ground-glass joint or polythene stopper; if a rubber stopper is used, it should first be boiled in concentrated NaOH solution and then in water.

The hydrogen gas for hydrogen electrodes must be as pure as possible.   That supplied commercially in cylinders is generally satisfactory, but it should be passed through wash-bottles containing (a) a solution of alkaline pyrogallol (2 g pyrogallol in about 35 ml $4N$ sodium hydroxide), (b) very dilute sulphuric acid, (c) water, and finally (d) a sample of the solution used in the cell.   Wash-bottle (d) is to ensure that the hydrogen stream does not alter the concentration of the solution in the cell.   It is advisable to avoid the use of rubber in connecting the gas train owing to its liability to contain sulphur compounds which may "poison" the electrode; polyvinyl chloride tubing is very satisfactory, and polythene can also be used. If rubber must be used, it should first be boiled in concentrated NaOH solution and then washed.   The apparatus must be air-tight.

Better removal of oxygen can be achieved by passing the hydrogen over palladized asbestos at 400° C or reduced copper wire at 600° C.   If cylinder hydrogen is not available, the gas can be made by a laboratory electrolytic generator or even by the action of pure hydrochloric acid on zinc, followed by purification.

Operation of hydrogen electrodes.   A steady stream of hydrogen should be bubbled through the cell until the electrode assumes a constant e.m.f.; this may take 10 to 20 minutes, and thereafter the e.m.f. should be independent of the rate of bubbling.   The correct value is not reached until oxygen has been removed.

Unfortunately, platinized platinum electrodes are susceptible to "poisoning"; that is to say, they sooner or later lose their catalytic activity, often as a result of adsorption of traces of substances such as arsenic, sulphur and mercury compounds on the active surface. The symptoms of poisoning are (i) irreproducibility, (ii) sluggishness in attaining a steady e.m.f., and (iii) dependence of the e.m.f. on the rate of bubbling of H_2.   If the platinum electrode becomes poisoned it must be cleaned and platinized again as already described.

Limitations.   Inorganic oxidizing agents (Fe^{+++}, $Cr_2O_7^{--}$, MnO_4^-, etc.) and various organic substances (e.g. alkaloids, per-acids, dyestuffs) are reduced by the hydrogen electrode; similarly, strongly reducing substances like stannous chloride, and metallic salts of Cu, Ag, Bi, Hg, etc. interfere.   Some colloidal materials inactivate the platinum.   It is seen, therefore, that these restrictions, together with the liability to poisoning and the precautions needed to obtain reliable results, tend to limit the practical usefulness of the hydrogen electrode.   It is employed chiefly in

accurate research work, while the more convenient quinhydrone or glass electrodes are used elsewhere.

EXPERIMENT

Determine the e.m.f. (25° C) of the cell H_2(Pt)|HCl, *molality* m|AgCl|Ag *with various concentrations of* HCl *from about* 0·1N *to about* 0·0001N, *and hence obtain the activity coefficients of* HCl.

Procedure. Prepare two (duplicate) hydrogen electrode half-cells (Fig. 12.11) and two silver–silver chloride electrodes (p. 259). Fill all four electrode vessels with the first solution of HCl. Since the above cell is one without liquid junction, no salt bridge is needed, and the two half-cells can be coupled together by a short length of polyvinyl chloride tubing containing the same HCl solution. Set up the cells in a thermostat at 25·0° C, and check the e.m.f. of the duplicates against one another. If they agree, measure the e.m.f. of the above cell, making sure that a steady value has been reached. Repeat with other concentrations of HCl. To expedite the work, the HCl solutions in bottles may be placed in readiness in the thermostat and a stream of H_2 passed through in order to remove most of the dissolved air. One cell can be prepared while the other is coming to equilibrium. The barometric pressure should be noted.

Calculation. The e.m.f. of the hydrogen electrode is given (p. 244) by $E_H = (RT/F) \log_e (a_{H^+}/p_{H_2}^{\frac{1}{2}})$ and that of the silver–silver chloride electrode by $E_{Ag/AgCl} = E^\circ_{Ag/AgCl} - (RT/F) \cdot \log_e a_{Cl^-}$. The net e.m.f. of the cell is $E_H - E_{Ag/AgCl} = -E^\circ_{Ag/AgCl} + (2 \cdot 303 RT/F) \log_{10} a_{H^+} \times a_{Cl^-}$. If only a few measurements can be made, one can assume the value of $E^\circ_{Ag/AgCl}$ (0·222 V) and calculate $a_{H^+} \times a_{Cl^-}$ which is equal to $m_+ f_+ m_- f_- = m^2 f_\pm^2$, (where m is molality, f activity coefficient) and hence obtain $f_\pm$ for the various solutions. Alternatively, $f_\pm$ for one of the solutions can be taken from other data.

If a number of accurate measurements can be made down to very low concentrations, the following treatment [1] can be applied, thus dispensing with auxiliary data. It is known that activity coefficients of 1 : 1 electrolytes follow a law of the form $\log_{10} f_\pm = -0 \cdot 5\sqrt{m} + Bm$. The e.m.f. of the cell (E) is equal to $-E^\circ_{Ag/AgCl} + 2RT/F \cdot \log_e mf_\pm$. Substituting and rearranging, $E - 0 \cdot 118 \log_{10} m + 0 \cdot 0591\sqrt{m} = -E^\circ_{Ag/AgCl} + 0 \cdot 118 Bm$. A graph of the left-hand side of this equation against m should therefore be a straight line which can be confidently extrapolated to $m = 0$, giving $E^\circ_{Ag/AgCl}$, and the slope of the line gives the constant B, from which the $f_\pm$ values of the electrolyte can then be calculated, according to the equation given above.

Other experiments. The hydrogen electrode may be used to determine the pH of buffer mixtures (p. 269). Thermodynamic dissociation constants of weak acids may be determined by extrapolation to zero ionic strength of results for buffer mixtures having different salt concentrations. For potentiometric titrations with the hydrogen electrode see p. 280.

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See monographs cited under Bibliography 12F.
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12E.   OXIDATION-REDUCTION ("REDOX") POTENTIALS

When platinum is immersed in a solution of a ferrous or ferric salt, or of some other reducing or oxidizing agent, a certain potential is established depending on the affinity of the ions for electricity or their tendency to pass from a higher to a lower state of oxidation. If, for example, one sets up a cell of the type, $Pt \,|\, Fe^{++} \,\|\, Fe^{+++} \,|\, Pt$, then on joining the two electrodes by a conductor, the ferrous ions will give up electrons to the electrode and thereby pass into the ferric state.   The electrons flow along the connecting wire and are taken up by the ferric ions, which thereby pass into the ferrous state.   The equilibrium state will be attained when the ratio of the activities of ferric and ferrous ions, $a_{Fe^{+++}}/a_{Fe^{++}}$, is the same at the two electrodes.

When a platinum electrode is placed in a solution containing ferric and ferrous ions, the potential of the electrode is given by the expression

$$E = E^\circ + \frac{2 \cdot 303 RT}{zF} \log_{10} \frac{a_{Fe^{+++}}}{a_{Fe^{++}}}$$

where z is the difference in valency of the ions and $a_{Fe^{+++}}$ and $a_{Fe^{++}}$ are the activities of the ferric and ferrous ions respectively.   Since $z = 1$, the above expression becomes, for the temperature of $15°$,

$$E = E^\circ + 0 \cdot 0571 \log_{10} a_{Fe^{+++}}/a_{Fe^{++}}$$

E° is the potential which is established when a platinum electrode is dipped in a solution in which the activities of ferric and ferrous ions are the same.   It is a measure of the tendency of the ion to pass from the higher to the lower state of oxidation.   The more positive the value of the oxidation–reduction ("redox") potential, the more effective is the ion in the higher state of oxidation as an oxidizing agent; and the more negative the oxidation–reduction potential, the more powerful is the ion in the lower state of oxidation as a reducing agent.

In many oxidation-reduction systems, hydrogen ions take part in the electrode reaction, and consequently the "redox" potential set up is dependent on the activity of hydrogen ions in the solution (see example of the quinhydrone electrode, p. 269), and the standard redox potential is that for a solution in which $a_{H^+} = 1$.

It generally happens that oxidation–reduction processes are studied

in the presence of acids or other electrolytes, and therefore the solution is usually one of *high ionic strength*.   Consequently, the ionic *activities*, especially of polyvalent ions such as Fe^{+++}, Ce^{++++}, etc. may differ considerably from *concentrations*.   Unfortunately, there is no satisfactory method for calculating activity coefficients of polyvalent ions in solutions of high ionic strength.   Standard redox potentials have sometimes been determined by extrapolating observed redox potentials to zero ionic strength.   These true standard potentials are of little practical significance, however, and it is more useful to report the so-called *formal oxidation–reduction potential*, obtained by taking concentrations instead of activities in the above equation.   Thus, for the $Fe^{+++}-Fe^{++}$ system,

$$E = E^{\circ}_{\text{formal}} + (RT/F)\log_e [Fe^{+++}]/[Fe^{++}]$$

The formal redox potential is not expected to be a true constant, but it is effectively constant for solutions of the particular ionic strength employed in, say, a redox titration.

Redox indicators.   Certain organic dyes which can undergo reversible oxidation–reduction exhibit different colours in the oxidized and reduced states.   In many cases the reduced form ("leuco" compound) is colourless.   Generally the reduction involves one or more hydrogen atoms and consequently the colour change of these dyes occurs at different redox potentials according to the pH of the solution.   For example, the redox potential at which methylene blue exists half in the blue form and half in the reduced (colourless leuco) form is $+0\cdot101$ V at pH 5, $+0\cdot011$ V at pH 7, and $-0\cdot050$ V at pH 9.

Redox indicators with different E° values (at a given pH) are available, and are used in biochemistry to determine the approximate oxidation–reduction conditions prevailing in biological systems.   For example, at a redox potential of $0\cdot2$ V and pH 7, phenol-*m*-sulphonate indo-2 : 6-dibromo phenol is colourless while thionine is violet; at $-0\cdot05$ V both these indicators are colourless, but indigo di-sulphonate is coloured. For biological purposes indicators are used having E° at pH 7 ranging from $+0\cdot35$ to $-0\cdot35$ V.

Examples of important oxidation–reduction systems which occur in living systems are: $2RSH \rightleftharpoons RSSR + H_2$, e.g. the cysteine–cystine system: various haemoglobin systems: biological oxidations involving "respiratory pigments", vitamin C, adrenaline, luciferin, and many pigments.[1]

Redox indicators are also employed in inorganic volumetric analysis.[2]

EXPERIMENT

Determine the formal redox potential of the ferrous–ferric system and of o-phenanthroline, and ascertain whether this indicator is suitable for use in the volumetric determination of ferrous salts.

Procedure.   Prepare (a) $N/10$ Fe^{++} solution and (b) $N/10$ Fe^{+++} solution by weighing out ferrous ammonium sulphate and ferric

alum respectively, both solutions to be made up in approximately N sulphuric acid solution.   Pipette out various proportions of solutions (a) and (b) into small beakers, thus obtaining various values of $[Fe^{+++}]/[Fe^{++}]$.

The platinum electrode consists of a square of platinum foil welded to a platinum wire which is mounted in a glass tube in the usual manner.   It is cleaned in concentrated nitric acid, washed, and then heated to redness in an alcohol flame.   The platinum electrode assumes the redox potential of the solution as soon as it is immersed in it.   To measure the potential one must, of course, have also a reference electrode.   Usually a calomel half-cell is used, and is connected to the beaker of solution by a saturated-KCl solution and agar bridge as in Fig. 12.8 (b).

Ortho-phenanthroline indicator solution is made by dissolving 0·23 g *o*-phenanthroline+0·12 g ferrous sulphate in 100 ml of water. The "end-point" for an indicator can be considered to be the solution in which the colour change from one extreme to the other has proceeded half-way, i.e. [oxidized form] = [reduced form].   This solution corresponds to the formal redox potential of the indicator. The potential may be found approximately as follows.   Add a little of solution (a) to some approx. N H_2SO_4 in a beaker, and then add 2 drops of the indicator solution.   "Titrate" the solution with an oxidizing agent (potassium dichromate or ceric sulphate) also dissolved in N H_2SO_4 until the indicator begins to change colour. By trial obtain about half the full intensity of colour.   Then, using this solution, determine the redox potential as described.

Calculation.   Compute the single electrode potential, E, assumed by the platinum electrode in each solution.   Plot a graph of E against $\log_{10}[Fe^{+++}]/[Fe^{++}]$.   This will be found to give a straight line, as indicated by the theory.   The slope of the line should be $2·303RT/(zF)$, and therefore gives z, the number of electrons transferred in the redox reaction. When $[Fe^{+++}] = [Fe^{++}]$, their ratio is unity and $\log_{10}[Fe^{+++}]/[Fe^{++}] = 0$. The redox potential where the line cuts the E axis is therefore $E°$, the formal standard redox potential of the Fe^{+++}–Fe^{++} system.

The suitability of the indicator for use in titrating ferrous solutions can be judged by calculating $[Fe^{+++}]/[Fe^{++}]$ for the redox potential at which the colour change has been observed to occur.

BIBLIOGRAPHY 12E: Oxidation–reduction potentials

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Applications of e.m.f. measurements

12F. pH DETERMINATION

The pH scale. The *hydrogen ion* plays a particularly important part in many processes and reactions—chemical, biological, and industrial. For example, extremely minute changes in the concentration of hydrogen ions may determine whether a metal will dissolve, or whether a metallic salt or a protein will precipitate. The determination and control of the concentration of hydrogen ions is therefore of the greatest importance in chemistry. The range of concentration which may be encountered is very great, extending from, say, a $1N$ solution down to pure water in which $[H^+] \approx 10^{-7}N$, and as far beyond into alkaline solutions. Thus, in a $1N$ NaOH solution, $[OH^-] = 1$, and since the ionic product of water, $[H^+][OH^-] = 10^{-14}$ is maintained, $[H^+] \approx 10^{-14}N$. Sörensen (1909) introduced the convenient *pH scale of hydrogen ion concentration*; on this scale, a solution having $[H^+] = 10^{-x} N$ is said to have a *pH of x*. Clearly, $pH = -\log_{10} [H^+] = \log_{10} 1/[H^+]$ and x is usually a positive number ranging from about 0 (for a $1N$ acid) through 7 (for a neutral solution) to about 14 (for a $1N$ alkali).

It is obvious that these infinitesimal (but vitally important) hydrogen ion concentrations cannot be determined by ordinary analytical means. In fact, all methods of determining pH are based directly or indirectly on the original method introduced by Sörensen, namely, e.m.f. measurements with the hydrogen electrode. Using Nernst's theory of electrode potential (p. 240), Sörensen took the e.m.f. of a hydrogen electrode having $p_{H_2} = 1$ atm to be given by

$$E_H = (RT/F) \log_e [H^+] = -0.0571 \times pH \text{ (at 15° C)}$$

Therefore the e.m.f. of a hydrogen electrode is directly proportional to the pH of the solution. In practice, various other methods are often more convenient to use than the hydrogen electrode for pH determination, but they all relate back to the above definition and basic method of determination.

The significance of pH. It is nowadays necessary to point out that Sörensen's pH scale suffers from a certain lack of precision which nevertheless scarcely detracts from its value in practical chemistry. There are actually two sources of uncertainty. In the first place, Sörensen originally intended pH to be related to hydrogen ion *concentration*, but his fundamental method of measurement—the hydrogen electrode—is now known to depend on thermodynamic *activities* rather than concentrations, i.e. $E_H \propto \log a_{H^+}$ (*not* $\log [H^+]$) and $a_{H^+} = [H^+]f_{H^+}$. In very dilute solutions —say, those having an ionic strength of less than $0.001N$— f_{H^+} is near enough to unity for a_{H^+} to be taken as $[H^+]$, but this is certainly not true in

concentrated solutions. Now the great value of pH comes in connection with *equilibria* involving the hydrogen ion, e.g. dissociation of weak acids or bases, and here again a_{H^+} is the quantity involved, rather than $[H^+]$. pH as measured by the hydrogen electrode therefore gives the quantity required. The original quantity defined by $-\log_{10}[H^+]$ is not only of little theoretical significance, but, in fact, it cannot be measured directly by any known means. It has therefore come to be accepted that

$$pH \equiv -\log_{10} a_{H^+}$$

Curiously enough, this definition is still lacking in precision. Strictly, single electrode potentials and single ion activities cannot be determined unambiguously. Thus, a cell without liquid junction such as that discussed on p. 262 measures in fact $a_\pm$, not a_+ and a_- separately. (For example, it is impossible to state unambiguously the concentration of a solution of HCl in which $a_{H^+} = 1$; one can but suppose that $f_{H^+} \approx f_{Cl^-} \approx f_\pm$ and hence $a_{H^+} \approx m f_\pm$, which would mean that m would have to be about $1 \cdot 2N$.) If, on the other hand, one attempts to get a_{H^+} from single electrode potentials derived from cells having liquid junctions, the uncertainty as to the value of the liquid junction potential limits the precision of the result. Most pH measurements are based on cells of the type

$$H_2(Pt)\,|\,\text{solution containing } H^+\,\|\,\text{satd. } KCl\,\|\,\text{calomel cell}$$
$$\quad\quad\quad\quad\quad\quad\quad\quad (a) \quad\quad\quad\quad\quad (b)$$
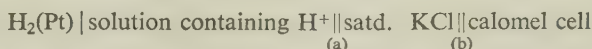
There are theoretical reasons (p. 245) for believing that the liquid junction (b) has negligible junction potential (say $< 0 \cdot 1$ mV), but there is no such assurance for junction (a) since such junctions are liable to contain significant concentrations of the highly mobile H^+ or OH^- ions. The degree to which saturated KCl does or does not "eliminate" such liquid junction potentials is uncertain. Consequently, the significance of pH values is uncertain to the same degree. Nevertheless, the value of the pH scale is not depreciated by this realization. Its practical usefulness is firmly established in many fields of applied chemistry, and fortunately, a high degree of precision is rarely, if ever, required.

At the present time the pH scale is accepted on its merits because it is empirically indispensable. pH is deemed to be defined by the method of measurement.[1] The pH value may be taken to be *very roughly* $= -\log_{10}[H^+]$; the higher the ionic strength, the greater the error in this assumption. Rather more accurately, $pH = -\log_{10}[H^+]f$, where f can be considered as the activity coefficient of a typical uni-univalent electrolyte in the appropriate solution. This interpretation is valid within $\pm 0 \cdot 02$ pH units for the range pH 2 to pH 12 in solutions of ionic strength not greater than $0 \cdot 1$ (i.e. f values between 1 and about $0 \cdot 75$). Outside these limits the precision of interpretation of pH decreases.

The significance of pH is discussed more fully by Dole[2] and by Bates.[3]

Buffer solutions. The pH of water and of very dilute solutions of salts is extremely sensitive to traces of impurities, such as dissolved CO_2, alkali derived from glass surfaces, etc. When a solution of definite pH is required, it is rarely satisfactory merely to add acid or

alkali until the desired pH is produced, because the pH of the resulting solution is unstable. Instead, "buffer mixtures" are used. These are solutions of considerable total concentration in which the pH is controlled by a chemical equilibrium. The constituents are weak acids (or bases) and their salts. When, for example, one adds a small quantity of hydrochloric acid to a mixture of acetic acid and sodium acetate, the hydrogen ions unite to a large extent with acetate ions to form un-ionized acetic acid, and the concentration of hydrogen ion is thereby prevented from increasing to any considerable extent. Similarly, when a small quantity of alkali is added to the mixture, the hydroxide ions react with the acetic acid to form acetate ions and water, and again the hydrogen ion concentration remains practically unchanged.

Numerous buffer mixtures have been recommended, including mixtures based on acetic, boric, citric, phosphoric, malonic, phthalic and oxalic acids and on ammonium salts, and any pH from 1 to 10 can be obtained by making up a suitable buffer solution.[4] The following are examples of mixtures giving integral pH values.

pH value	Composition of mixture
1	47·5 ml $N/5$ HCl+25 ml $N/5$ KCl; mixture dil. to 100 ml.
2	5·3 ml $N/5$ HCl+25 ml $N/5$ KCl; mixture dil. to 100 ml.
3	20·55 ml $M/5$ Na_2HPO_4+79·45 ml $M/10$ citric acid.
4	41·0 ml $M/5$ acetic acid+9·0 ml $M/5$ sodium acetate.
5	14·75 ml $M/5$ acetic acid+35·25 ml $M/5$ sodium acetate.
6	9·0 ml $M/5$ acetic acid+191·0 ml $M/5$ sodium acetate.
7	12·0 ml $M/20$ borax+188·0 ml. of a solution containing 12·40 g H_3BO_3 and 2·93 g NaCl in 1 litre.
8	11·0 ml $M/20$ borax+29·0 ml of a solution containing 12·40 g H_3BO_3 and 2·93 g NaCl in 1 litre.
9	40·0 ml $M/20$ borax+10·0 ml of a solution containing 12·40 g H_3BO_3 and 2·93 g NaCl in 1 litre.
10	Equal parts of $M/40$ $NaHCO_3$ and $M/40$ Na_2CO_3.

Four other solutions of accurately known pH, which can be made up readily from single substances, are given on p. 275.

Since the dissociation constants of ammonium hydroxide and acetic acid are identical, solutions of ammonium acetate provide valuable neutral buffer solutions with pH = 7·0, and the pH remains constant over a wide range of concentrations. The solutions should not be prepared from the salt but by mixing together equal volumes of accurately prepared $2N$ solutions of ammonium hydroxide and acetic acid. Dilution of this normal solution does not alter the pH.

Determination of pH with the hydrogen electrode. The cell usually employed is of the type

$$H_2(Pt) \,|\, \text{solution of unknown pH} \,\|\, \text{satd. KCl, } Hg_2Cl_2 \,|\, Hg$$

i.e. a hydrogen electrode operating in the solution is connected to a saturated KCl calomel electrode, either by dipping the calomel electrode vessel (Fig. 12.7) directly into the solution or via a saturated KCl bridge (conveniently, an agar bridge, p. 253). In place of a saturated KCl calomel electrode one may use a N KCl calomel or a silver–silver chloride electrode (p. 259). The hydrogen electrode is prepared as previously described (p. 260), and should be contained in a vessel such as that shown in Fig. 12.11 or Fig. 12.3 (a). If the e.m.f. of the calomel or other reference electrode is $E_{\text{ref.}}$ on the standard scale, the e.m.f. of the hydrogen electrode, E_H, is (e.m.f. of cell $- E_{\text{ref.}}$), and the pH can be calculated from the equation

$$E_H = -2 \cdot 303 (RT/F) \times \text{pH}$$

Thus, at 18° C, using a saturated calomel electrode ($E_{\text{ref.}} = 0 \cdot 249$ V), the pH of the solution may be computed from the formula

$$\text{pH} = \frac{\text{e.m.f. (measured)} - 0 \cdot 249}{0 \cdot 0578}$$

The hydrogen electrode, which has an accuracy, at constant temperature, of $0 \cdot 02$ pH (p. 260) should not be used in the presence of oxidizing agents, of metals which lie below hydrogen in the electromotive series (e.g. copper, silver), or of organic compounds which undergo hydrogenation. It is unsuitable for use, also, in presence of colloids.

EXPERIMENT

Determine the pH of a given solution.

The pH of the buffer solutions given above may be tested, or the pH of mixtures of $N/20$ acetic acid and $N/20$ sodium acetate solutions in different proportions may be measured. In the latter case, it may be shown that the pH is approximately linear with $\log_{10}$ [sodium acetate]/[acetic acid] in the mixtures (p. 287).

The quinhydrone electrode.

Theory. Biilmann (1921) introduced the use of the quinhydrone electrode for pH determinations. This electrode is a redox electrode at which the reversible reaction

$$\underset{\text{quinone (Q)}}{C_6H_4O_2 + 2H^+} = \underset{\text{hydroquinone (QH}_2)}{C_6H_4(OH)_2 - 2\ominus}$$
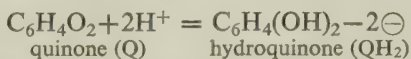
takes place. The electrode potential (p. 263) is given by

$$E = E_Q^\circ + \frac{RT}{2F} \log_e \frac{a_Q \cdot a_{H^+}^2}{a_{QH_2}}$$

where a_Q and a_{QH_2} are the activities of quinone and hydroquinone respectively in the solution, and E_Q° is the standard electrode potential of the quinhydrone electrode. In practice the ratio a_Q/a_{QH_2} is maintained constant at unity by saturating the solution with the substance "quinhydrone", which is a 1 : 1 molecular compound of these substances. The potential of such a quinhydrone electrode is then

$$E = E_Q^\circ + RT/F \log_e a_{H^+} = E_Q^\circ - (2 \cdot 303 RT/F)\text{pH}$$

The electrode can therefore be used to measure pH in the same way as the hydrogen electrode. The value of E_Q° is given by the expression[5] $0 \cdot 699 - 0 \cdot 0007_4 \ (t - 25)$ V.

Advantages and limitations. The quinhydrone electrode is extremely simple to set up, and it gives its true reversible potential immediately. It is applicable to many types of solution and gives pH values as accurately as the hydrogen electrode. It can sometimes be used in solutions containing reducible substances (e.g. dilute HNO_3, NO_3^-, Cu^{++}, Pb^{++}, Cd^{++}, unsaturated acids, alkaloids) where the hydrogen electrode is not applicable. Very small quantities of solution suffice for a measurement, and air need not be removed. On the other hand, the electrode cannot be used with solutions containing any substances which might react with quinone or hydroquinone (e.g. ferrous salts, manganese dioxide, aniline, boric acid, some proteins). Also, inaccurate results are obtained in solutions more alkaline than pH 8·5 because the hydroquinone begins to ionize as a weak acid. Further, in alkaline solutions quinhydrone slowly decomposes and undergoes oxidation from the air, resulting in a rising pH.

The quinhydrone electrode is subject to "salt error" when the concentration of electrolyte is greater than about $0 \cdot 1 M$. This defect can be overcome by saturating the solution not only with quinhydrone but also with quinone or hydroquinone.[6] In the former case, $E^\circ = 0 \cdot 75$ V and, in the latter case, $0 \cdot 619$ V, at 18°. It is advisable to have a small well at the bottom of the electrode vessel into which the solids settle and surround the platinum electrode.

EXPERIMENT

Determine the pH of a number of buffer solutions (as on p. 268) or carry out a potentiometric titration (p. 287).

Practical Details. The cell employed takes the form

Pt | quinhydrone (satd.) in solution of unknown pH ‖ satd.
KCl salt bridge ‖ reference electrode
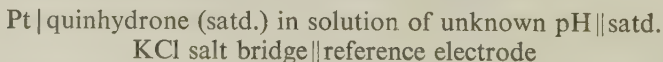
The platinum electrode is a bright foil (p. 265). The solution under test is contained in a small beaker, and pure quinhydrone is added

in sufficient quantity to leave some in excess (1–2 g per 100 ml of solution). The salt bridge is conveniently an inverted U-tube containing KCl—agar jelly (p. 253). The reference electrode may be a saturated KCl calomel half-cell or a N or $N/10$ KCl calomel or Ag/AgCl electrode. If the e.m.f. of the reference electrode is $E_{ref.}$, then $E_{observed} = E_{quin.} - E_{ref.} = E_Q^\circ - (2 \cdot 303RT/F)\text{pH} - E_{ref.}$. Hence,

$$\text{pH} = \frac{E_Q^\circ - E_{ref.} - E_{observed}}{2 \cdot 303RT/F}$$

For example, with a saturated calomel electrode and at a temperature of 18° C,

$$\text{pH} = \frac{0 \cdot 455 - E_{observed}}{0 \cdot 0578}$$

A particularly convenient reference electrode for the present purpose is another quinhydrone electrode in a solution of known pH. Veibel [7] recommended the use of quinhydrone in "standard acid mixture", i.e. a solution $0 \cdot 01N$ in HCl and $0 \cdot 09N$ in KCl. A quantity of this mixture can be kept in stock, and when a cell is to be made up, a little quinhydrone is simply added to a portion of the mixture, and a bright platinum wire inserted. The solution should be renewed, and the electrode cleaned, daily. The pH can be taken as 2·08. Quinhydrone in $M/20$ potassium hydrogen phthalate (pH = 4·00) is another convenient reference electrode.[8] The e.m.f. of a cell composed of two quinhydrone electrodes in solutions of different pH is simply

$$(2 \cdot 303RT/F)(\text{pH}_1 - \text{pH}_2)$$

The glass electrode. Haber and Klemensiewicz (1909) showed that if a thin membrane of glass is used to separate two solutions, it develops a membrane potential which is dependent chiefly on the pH of the solutions. This principle forms the basis of a valuable method of measuring pH. The cell employed is of the form

| Reference electrode (1) in solution (1) | Glass membrane | solution (2), pH = x | satd. KCl salt bridge | reference electrode (2). |

The precise e.m.f. of the cell is not of particular interest because it includes an indefinite "asymmetry potential" (perhaps due to strain) which generally exists across the glass membrane even if the two sides of the cell are of identical composition. However, this asymmetry potential is practically constant. If, therefore, measurements are made with all parts of the cell unchanged except solution (2), it is found that the total e.m.f. varies in the manner expected for a similar cell containing a hydrogen electrode, i.e.

$$E = \text{const.} + (2 \cdot 303RT/F) \log_{10} a_{H^+} = \text{const.} - (2 \cdot 303RT/F)\text{pH}$$

In practice, the glass electrode assembly is *calibrated* by measuring first the e.m.f. of the cell with solution (2) of known pH. This

solution is then replaced by the solution of unknown pH. The *change of e.m.f.* is given by

$$\Delta E = (2 \cdot 303 RT/F)(\text{pH}_1 - \text{pH}_2)$$

It is clear that any types of reference electrode can be used on the two sides of the cell; their e.m.f., since they do not enter into the final expression, need not be known, but must be constant from one reading to another. Usually electrode (1) is a silver–silver chloride electrode in dilute HCl and electrode (2) is a satd. KCl calomel half-cell.

Various forms of glass electrode have been used. That most commonly employed (Fig. 12.12) consists of a thin-walled soda glass, *D*. The bulb contains a small silver–silver chloride wire elec-

FIG. 12.12. Glass electrode assembly (Morton pattern).

trode in dilute acid, the tube being sealed at the top. New glass electrodes should be soaked for a period in dilute HCl and thereafter always stored in distilled water. The bulb may be simply suspended in a small beaker of the solution to be tested, but it is better to use an assembly such as that of Morton[9] (Fig. 12.12) which ensures adequate protection to the electrode. The solution is poured through the funnel, *H*, into the compartment, *A*. Connection is made to a calomel electrode *C* by a tube *F* containing saturated KCl solution. A three-way stopcock *S*, permits the solution to be drained from *A* or brought into contact with the KCl solution. The KCl bridge can also be flushed to waste. The e.m.f. measurement is made with the tap *closed*; the surfaces of the tap are not greased and therefore conduct electrically in the thin film of solution. Another glass electrode assembly is shown in Fig. 12.13 (a).

The calomel electrode may be of any type. A compact form suitable for dipping direct into the test solution is often used. It is permissible to use a very small calomel electrode in work with the glass electrode because only a minute current is drawn from the cell during the measurements (see below) and consequently the danger of polarizing the electrode is negligible. Although it is traditional to use a calomel electrode for reference electrode (2), a simpler and more compact dipping electrode is a silver–silver chloride wire

(similar to that inside the glass electrode bulb) in a tube containing saturated KCl.   (See Fig. 12.13 (b).)

Measurement of glass electrode potentials: valve electrometers.

Glass electrodes generally have a resistance of the order of 10^7–10^8 Ω. Since it is necessary to measure the electrode potential to better than 1 mV for an accuracy of 0·02 pH units, the instrument for detecting the balance point of the potentiometer must be sensitive to less than 10^{-10}–10^{-11} amp. This is too small a current to be detected by ordinary galvanometers. Early workers used quadrant electrometers, but nowadays thermionic valve circuits are always employed for pH measurements with glass electrodes. It is a characteristic of the triode valve that a substantial anode current (I_a) can be controlled by small changes of grid voltage, and relatively little current is drawn from the grid. The grid current I_g can be reduced to about 10^{-15} amp in special types of *electrometer valve* (or even in some more common types of valve, operated at low voltages.[10]   The mutual conductance of such valves is low—for example, 5×10^{-5} amp (anode current) per volt (on grid)—but is sufficient

FIG. 12.13. Arrangement for potentiometric titration with a glass electrode.
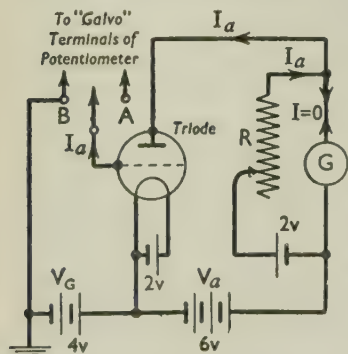
FIG. 12.14. Principle of the valve-voltmeter.

cient to give a measurable current sensitivity. Thus, a change of grid voltage of 1 mV would produce a change in I_a of 5×10^{-8} amp, which can be detected by a reasonably robust galvanometer. However, under these working conditions the valve passes a considerable total anode current (*c.* 40 μA), and it is therefore necessary to provide an adjustable voltage to "back off" this current so that the galvanometer detects only *changes* of anode current.

The principle of the valve electrometer circuit can be followed from Fig. 12.14. The grid is connected first to the point B, and the rheostat R is adjusted until no deflection is observed on the galvanometer G. The grid connection is then switched to point

P.P.C.—18

A. If *A* is not at the same potential as *B* a change of anode current results, producing a deflection of *G*. If the points *A* and *B* are connected to the "galvanometer" terminals of an ordinary potentiometer, the circuit serves as indicator of the point of balance of the potentiometer, for, on adjusting the potentiometer so that no deflection of *G* results on switching from *A* to *B*, one knows that these points are at the same potential and consequently the e.m.f. of the cell can then be read in the usual way from the potentiometer dials.
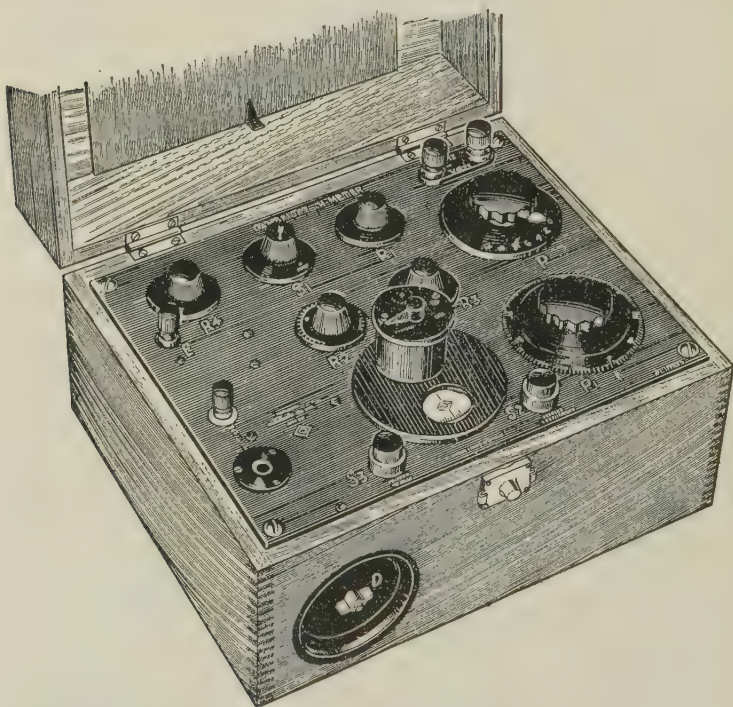
Fig. 12.15. pH-meter (null-deflection, bench pattern).
(Courtesy Cambridge Instrument Co. Ltd., London.)

A valve electrometer can be used in this way to adapt an ordinary potentiometer for work with glass electrodes. More often, however, a potentiometer and valve voltmeter are combined into a single instrument, the dials of which are graduated in terms of pH instead of mV, and a rheostat is provided for balancing out the asymmetry potential of the glass electrode. Such instruments are known as *pH-meters*.

pH-meters. Two types of pH-meter are in common use. The null-deflection type (Fig. 12.15) consists essentially of a potentiometer combined with an electrometer valve in the manner explained above. It has the merits of simplicity, accuracy (better than 0·01 pH),

stability, and almost unlimited life. An instrument of this type, operated from large accumulators, is the most satisfactory for a chemical laboratory. The maker's instructions must be consulted for the method of operation, but the principles involved should be clear from the above explanation.

In the second type of pH-meter, the anode current from the electrometer valve is amplified by a circuit designed to give an output current which is linear with the grid voltage. The result is registered on a robust pointer meter which can be calibrated directly in pH units. Such pH-meters, which are generally mains operated, are "direct reading" and are therefore particularly useful in industry, but they are less accurate than the null type, and in other ways are less suitable for laboratory work unless a very large number of solutions is to be handled.

It is important to connect pH-meter circuits to earth at the point B and to use screened leads between the electrodes and the meter in order to avoid capacity effects. Difficulty is also sometimes experienced, particularly in humid weather, owing to leakage currents; the trouble can often be removed by standing the pH-meter and the electrode assembly on flat blocks of paraffin wax.

Standardization of glass electrodes. All pH-meters have provisions for standardizing the glass electrode in a buffer solution of known pH. This is necessary because different electrodes have different asymmetry potentials. Once the adjustment has been made, so that the meter registers correctly the known pH of the buffer solution, the instrument gives the pH of other solutions without any calculation. The standardization should be checked occasionally.

The following buffer solutions have been recommended for standardizing glass electrodes.[1]

pH standards for glass electrodes (25° C)*

For pH range		Buffer solution	g per litre	pH
3—10	A	0·05 M potassium hydrogen phthalate	10·21	4·00$_5$
	B	0·05 M borax	19·07	9·18
< 3	C	0·01 M potassium tetroxalate ($2H_2O$)	2·54	2·15
>10	D	0·01 M trisodium phosphate ($12H_2O$)	3·80	11·72

* Only slightly dependent on temperature; solution A becomes 4·01 at 38° C, and 4·10 at 60°.

If the electrode is standardized with solution A, it can be tested for satisfactory functioning by measuring the pH of solution B. If

very acid or very alkaline solutions are to be studied, it is better to standardize with C or D respectively in order to minimize the errors to which the glass electrode is liable at extreme pH values (see below).

After an electrode has been standardized, it is rinsed with water and then with the solution to be studied, the pH of which is read at once. If the electrode is then washed again and returned to the first buffer it should, of course, give the correct pH again. If it does not, a perforation of the electrode should be suspected. Solutions A and B should then be used for checking the reproducibility of the electrode.

Limitations of the glass electrode. Ordinary glass electrodes function satisfactorily from pH 0 to pH 9, and can be used even in unbuffered solutions in the range 6 to 8 provided the solution is agitated with a stream of nitrogen to remove CO_2 and to condition the electrode surface. As the pH is increased above 9 they begin to give results which are increasingly too high compared with those given by a hydrogen electrode in the same solutions. The error at high pHs is found to depend particularly on the *sodium* ion concentration; for example, at pH 12 the electrode might read 12·8 in a solution which is $0·01N$ in respect to Na^+. The "alkali error" depends on the temperature, type of glass, composition of solution, etc. The standardization of the asymmetry potential of the electrode may also be disturbed by strong alkali. In recent years a special glass electrode has been introduced for the range pH 9–14, but high accuracy cannot be expected with it.

Glass electrodes are also subject to errors in highly acid solutions, at high temperatures, in concentrated alcohol solutions, and in the presence of ionized colloids.

EXPERIMENTS

(1) *Test the functioning of a glass electrode.* Measure the pH of a number of buffer solutions of pH ranging from 1 to 11·7 (p. 269), noting particularly the reproducibility of the results on transferring the electrode from buffers of high pH to those of lower pH.

(2) *Investigate the "salt effect" on pH.* Determine the effect of KCl on the pH of solutions of HCl. Prepare $0·01N$ HCl and add to portions of it various amounts of KCl, by weight, up to $0·1N$. Determine the pH with a glass electrode calibrated on buffer C. Since $pH \approx -\log_{10} [H^+] f_{\pm}$, the effect of ionic strength, μ, on $f_{\pm}$ can be obtained approximately, taking $f_{\pm}$ for pure $0·01N$ HCl as $0·906$. Plot $\log f_{\pm}$ against $\sqrt{\mu}$ (cf. p. 242).

(3) *Determine the degree of hydrolysis of aniline hydrochloride.* Prepare $N/20$, $N/40$, $N/80$ and $N/160$ solutions of aniline hydrochloride, and determine their pH values with a glass electrode.

Preparation of aniline hydrochloride. Pass dry HCl gas (made by dropping conc. HCl into conc. H_2SO_4 *in a fume cupboard*) through a 10%

solution of aniline in dry ether. Filter off the precipitated hydro-chloride, wash with dry ether, and store in a desiccator over KOH.

Calculation. The hydrolysis reaction is $C_6H_5NH_3^+Cl^- = C_6H_5NH_2 + H^+Cl^-$. If x is the degree of hydrolysis, the classical hydrolysis constant, K_h, is given by $x^2c/(1-x)$, where c is the overall concentration of aniline hydrochloride. The thermodynamic hydrolysis constant would be $a_{C_6H_5NH_2} \times a_{H^+}/a_{C_6H_5NH_3^+}$ which is practically the same as the classical expression since $f_{C_6H_5NH_2} \approx 1$ and $f_{H^+} \approx f_{C_6H_5NH_3^+}$, and the only correction needed is to allow for the fact that $pH \approx [H^+]f_{\pm}$. The value of $f_{\pm}$ can be estimated approximately (p. 242).

The dissociation constant of aniline as a base, $C_6H_5NH_2 + H_2O = C_6H_5NH_3^+ + OH^-$, is $K_b = [C_6H_5NH_3^+][OH^-]/[C_6H_5NH_2]$, and hence $K_h = K_w/K_b$, where K_w is the ionic product of water ($= 0.6 \times 10^{-14}$ at $18°$ C). Hence K_b can be calculated approximately.

(4) *Other experiments:* as for hydrogen and quinhydrone electrodes (pp. 268—70). For potentiometric titrations with a glass electrode, see p. 287.

pH determination with indicators. It is convenient to include in this section on pH measurements a short account of the use of *indicators* for approximate pH determination. pH indicators are weak acids or bases which exhibit different colours in their ionized and unionized states. For example,

$$\text{methyl orange acid} \rightleftharpoons \text{methyl orange anion} + H^+$$
$$\text{(red)} \qquad \qquad \text{(yellow)}$$
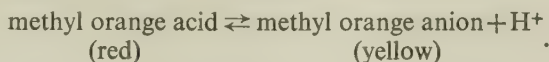
The dissociation constant, K_a, is given by $K_a = [\text{anion}][H^+]/[\text{acid}]$ and hence $pH = pK_a + \log_{10}[\text{anion}]/[\text{acid}]$, where $pK_a = -\log_{10} K_a$. If pK_a (which is a constant at a given temperature) is known, the pH of a solution can be determined by measuring the proportions of the two forms of the indicator which are present when the indicator comes to equilibrium with the solution. The pK_a values for a number of common indicators may be read from the table below.

There are several methods of using indicators to determine approximately the pH of solutions; they all depend on colour matching. Visual colour matching is accurate to about 0.1 pH unit. Rather better accuracy is obtainable with a photoelectric colorimeter.

(1) A very rough figure is obtained by observing the colour formed with a "universal indicator", which consists of a mixture of indicators which goes through a series of colour changes with pH.

(2) The colour formed by adding a suitable indicator to the test solution is matched against a series of buffer solutions of known pH to which the same quantity of the same indicator has been added. For routine testing, sets of coloured glasses are obtainable, thus obviating the need for buffer solutions.

(3) Instead of using known buffer solutions, the colour obtained

with the unknown solution may be matched against the shade produced by combining the acid and alkaline colours of an indicator of known characteristics in variable proportions by means of an optical device. (Gillespie's method.[11]) The acid and alkaline forms of indicator are contained in separate vessels, and the variable proportions may be produced either by putting different concentrations of indicator in the two vessels, or by using a wedge cell apparatus. The first method has the merit of simplicity since no special apparatus is needed beyond a set of similar test-tubes and a wooden block bored to receive three pairs of tubes side by side. Horizontal holes make it possible to view the colour exhibited on looking through a pair of tubes (Fig. 12.16). This simple device facilitates comparison of the colours.

The indicator method of determining pH is not suitable for un-

FIG. 12.16. Wooden mount for determination of pH of solutions by the visual indicator method.

buffered solutions, for high salt concentrations (owing to a "salt error"), or for colloidal solutions which interact with the indicator.

EXPERIMENT

Determine approximately the dissociation constant of benzoic acid by measuring the pH of mixtures of benzoic acid and sodium benzoate by means of Gillespie's indicator method.

Method. Prepare 250 ml of solutions of benzoic acid and of sodium benzoate. Their concentrations should be about equivalent and should be obtained to an accuracy of about 1% by weighing out the dry substances. (Note that the solubility of benzoic acid is only about 0·3 g per 100 g of water at 20° C.)

Mix equal volumes of the solutions and determine the approximate pH of the mixture by adding one drop of universal indicator, comparing the colour produced with the published table for the indicator mixture. This result enables the best indicator for the experiment to be chosen (see list on p. 279).

Dilute some of the stock solution of indicator 10 times, and divide it into three portions: add one drop of concentrated HCl to one lot and one drop of concentrated NaOH solution to another, thus converting them entirely into the acid and alkaline forms respectively, while maintaining equal concentrations.

Select 24 test-tubes of about the same diameter (about $\frac{5}{8}$ in) and after thoroughly cleaning and drying them, pipette 15 ml of distilled water into 18 of them, and then add to different tubes 1, 2, 3, . . .

8 or 9 drops of acid indicator or alkaline indicator. The drops should be delivered from a fine dropping tube and under good control so that the drop size is constant.

Arrange the tubes in pairs such as 1-drop acid with 9-drop alkali, 2 acid with 8 alkali, etc., so that on looking through a pair of tubes one sees always the same density of dye (i.e. 10 drops in 2 tubes), but in different acid/alkali ratios.

Now prepare an accurate 1 : 1 mixture of the standard benzoic acid and sodium benzoate solutions. Pipette two separate 15 ml lots into separate tubes and add 5 drops of the neutral diluted batch of indicator to each.

Table showing pH for pairs of tubes in Gillespie's indicator method

Drop ratio	Brom-phenol blue	Methyl red	Brom-cresol purple	Brom-thymol blue	Phenol red	Cresol red	Thymol blue
1 : 9	3·1	4·05	5·3	6·15	6·75	7·15	7·85
2 : 8	3·5	4·4	5·7	6·5	7·1	7·5	8·2
3 : 7	3·7	4·6	5·9	6·7	7·3	7·7	8·4
4 : 6	3·9	4·8	6·1	6·9	7·5	7·9	8·6
*5 : 5	4·1	5·0	6·3	7·1	7·7	8·1	8·8
6 : 4	4·3	5·2	6·5	7·3	7·9	8·3	9·0
7 : 3	4·5	5·4	6·7	7·5	8·1	8·5	9·2
8 : 2	4·7	5·6	6·9	7·7	8·3	8·7	9·4
9 : 1	5·0	5·95	7·2	8·05	8·65	9·05	9·75

* Figures on this line are approximate values of the pK_a of the indicators.

Place these two tubes one behind the other in the comparator block and match the colour observed against the variable acid/alkali pairs. When the best match has been obtained, refer to the accompanying table to read off the pH. With care, it may be possible to interpolate and match to ±0·1 pH unit.

Repeat the pH determination on 2 : 1 and 1 : 2 mixtures of benzoic acid and sodium benzoate.

Calculation. For a weak acid buffer solution:

$$\text{pH} = \log_{10} \frac{1}{K_a} + \log_{10} \frac{\text{[salt]}}{\text{[acid]}}$$

where K_a = dissociation constant of the acid. If the three mixtures give concordant values of K_a, take a mean, but if not, repeat with other mixtures. Note that, as an error of 0·1 pH unit corresponds to a 30% error in K_a, the indicator method is not suitable for obtaining dissociation constants accurately.

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12G. POTENTIOMETRIC TITRATIONS

Theory.   Since the potential of an electrode dipping in the solution of an electrolyte depends on the concentration of the ions with which the electrode is in equilibrium, it is possible to use determinations of the potential as an "indicator" in volumetric analysis.   The electrode potential depends on the *logarithm* of the concentration of ions, and is therefore not suitable for obtaining concentration directly with any accuracy, but the change of potential with concentration *during a titration* provides an accurate indication of the equivalence point.   Thus, the cell

$$H_2(Pt) \,|\, \text{acid solution} \,|\, KCl aq. \,|\, \text{calomel electrode}$$

will have a certain e.m.f. depending on the pH of the solution.   On adding small portions of a standard solution of alkali to the acid, the e.m.f. of the cell will alter slowly at first, because the change in the electrode potential depends on the *fraction* of hydrogen ion removed.   As the amount of alkali added approaches equivalence to the amount of hydrogen ion in the solution, the fraction of the hydrogen ion concentration removed by each drop of alkali solution rapidly increases, and there is a correspondingly rapid change in the e.m.f.   Later, as excess of alkali is added, the e.m.f. again shows a slow change.   Consequently, when the e.m.f. of the cell, E, is plotted against the volume, v, of standard alkali added, a curve of the form shown in Fig. 12.17 is obtained.   The end-point of the titration is given by the point of inflection on the curve.   The point of inflection can be most easily found by plotting the values of $\Delta E/\Delta v$ against volume of titrating solution.   At the point of inflection the value of $\Delta E/\Delta v$ is a maximum.

In carrying out the titrations, the titrating liquid is run, in small

quantities at a time, from a burette into the solution to be titrated, the solution being kept well mixed by means of a stirrer. As the titration approaches the equivalence point, the titrating liquid is added in smaller and smaller amounts so that the graph in the neighbourhood of the equivalence point is obtained with precision.

Advantages. (1) Potentiometric titrations are applicable to any reactions for which an appropriate electrode is available; for example, sulphides can be titrated with lead salts, using a lead electrode. Many reactions for which no colour indicator is available can be employed in the potentiometric method.

(2) The determination is very reliable, since the result depends on a number of independent readings, not on one subjective judgment of an "end-point" (which may be rather ill-defined in indicator titrations). This is particularly important in research work when the quantity of material available is limited.

(3) An accuracy comparable with that of the best gravimetric analysis can be achieved if weight-burettes are employed instead of volumetric burettes, and the potentiometric titration is more rapid.

(4) Potentiometric titrations can be carried out on a micro scale with little difficulty and can often be ex-

Fig. 12.17. Potentiometric titration curve.

tended to extremely dilute solutions which would be beyond the sensitivity of conventional volumetric analysis.

Technique: simplified potentiometry. The obvious method of carrying out potentiometric titrations is to set up a cell, one electrolyte of which is to be titrated, and to determine its e.m.f. accurately in the usual way with a potentiometer after each addition of titrant. While this is most satisfactory, it is possible to dispense with a precision potentiometer since the highest accuracy of e.m.f. measurement is not needed. Fig. 12.18 shows a simple arrangement requiring only two wire-wound rheostats (coarse and fine), a millivoltmeter (shunted if too sensitive), a galvanometer, and a tapping key. The rheostats are adjusted until, on closing the key, no deflection is produced on the galvanometer. The millivoltmeter then reads the e.m.f. of the cell directly.

Another method, and one particularly suitable for potentiometric titrations since no balancing is needed at each reading, is the use of

a valve voltmeter.   The principle of the valve voltmeter has been explained in connection with the pH-meter (p. 273), where its use is obligatory because of the high resistance.   In potentiometric titrations with other electrodes one does not need to use an expensive electrometer valve with its low mutual conductance.   Since a grid current of up to about 10^{-6} amps would not cause excessive polarization of the electrodes, any ordinary triode can be used in a null-deflection valve-voltmeter circuit; with a bias of -2 V, the grid current is about 10^{-8} amps.

FIG. 12.18. Simple substitute for a laboratory potentiometer.

A more convenient method, however, is to employ a circuit in which the anode current is closely proportional to the grid voltage so that it is only necessary to note a deflection on a meter connected in the anode circuit.   Fig. 12.19 shows such a circuit, due to Garman and Droz,[1] which is easily constructed and gives very satisfactory performance.   The valves have been chosen to operate from dry batteries, to consume very little current, and to retain operating characteristics unchanged over a long period.   The valve is a battery
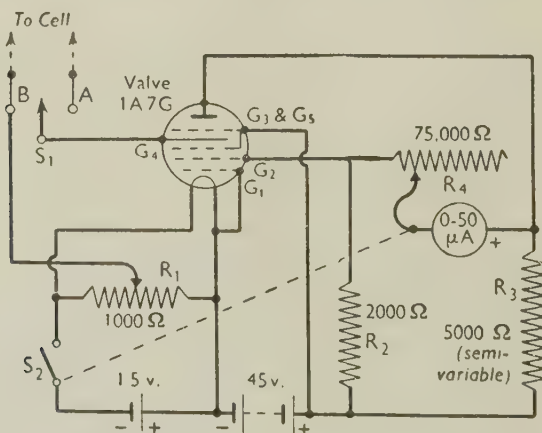
FIG. 12.19. Valve-voltmeter titrimeter of Garman and Droz.

pentagrid frequency changer (type 1A7G).   A 0–50 microammeter measures the out-of-balance current of a Wheatstone bridge circuit composed of R_2, R_3, and the effective resistances between cathode and grid 2 (R_{CG}) and grid 2 to anode resistance (R_{GA}).   The latter arms of the bridge are changed to different extents by alterations of the potential

of grid 4; as G_4 becomes more negative, R_{CG} decreases and R_{GA} increases. Provided a suitable R_2/R_3 ratio is used for the individual valve, it is possible to find a bias for G_4 (by adjustment of R_1, switch S_1 being connected to B) so that the bridge is balanced and the meter gives no deflection. On switching S_1 to point A, any difference of potential between A and B produces a proportionate deflection on the meter. The sensitivity of the meter can be controlled by altering R_4. At maximum sensitivity full-scale deflection is produced by about 120 mV potential on A. If the instrument is to be used as a valve voltmeter it is only necessary to choose a setting of R_4 which gives full-scale deflection with the required range of e.m.f. and then to prepare a calibration graph of meter reading against grid potential (varied by battery and potential divider across AB and read on a reliable millivoltmeter or potentiometer). The calibration graph is linear. The grid current is only about 10^{-10} amp, which is entirely negligible for all ordinary electrodes except the glass electrode. Tiny electrodes can therefore be used, and the cell may include in its electrical path closed (but ungreased) stop-cocks. This is often convenient for separating the various electrolytes.

WARNING: The microammeter may be damaged by excessive current if care is not exercised in using the instrument. The switch S_2, which turns on the power, is deliberately coupled to R_4 so that the instrument switches on in its least sensitive condition (R_4 maximum). The sensitivity should not be increased before trial has proved that neither position of S_1 can cause excessive current to flow through the meter.

Operation as a titrimeter. During a potentiometric titration the cell e.m.f. changes from, say, E_1 to E_2. In order to secure maximum accuracy over this range, one can balance the bridge for no deflection at grid potential E_1 (by connecting S_1 to A, and adjusting R_1) and then find a setting of R_4 at which E_2, the potential at the end of the titration, gives almost full-scale deflection. Clearly, a preliminary titration is needed to find the correct settings, R_1 being adjusted for zero deflection at the beginning of the final titration and R_4 being adjusted for full-scale deflection at the end. The accurate titration can then be carried out without touching the settings of R_1 and R_4.

Other valve-voltmeter circuits have been proposed by numerous authors.[2] For routine work, as in industry, it is often advisable to use multiple-valve circuits operated from the mains and incorporating robust meters, but for laboratory use it is almost always better to *choose the simplest method capable of giving satisfactory results.* The temptation to add elaborate electronic "refinements" is nowadays severe; it should be firmly resisted!

For routine electrometric titrations, the Mullard mains-operated valve voltmeter is very satisfactory (Fig. 12.20). This instrument employs a "magic eye" null-point indicator. It is sensitive to 2 mV, reads up to 2 V, and has an input impedance of > 20 MΩ.

Finally, it may be mentioned that in a few cases potentiometric titrations can be carried out by simply measuring the current which flows when the cell is allowed to discharge slowly through a high resistance.[3] The method, however, is of very limited applicability.

Differential potentiometric titrations. It has been mentioned that the point of inflection on a potentiometric titration (E against v) curve, which gives the equivalence point, can be most accurately located by plotting a graph of v against $\Delta E/\Delta v$ where ΔE and Δv are the increments of e.m.f. and of volume respectively at each addition during the titration. The graph takes the form shown in
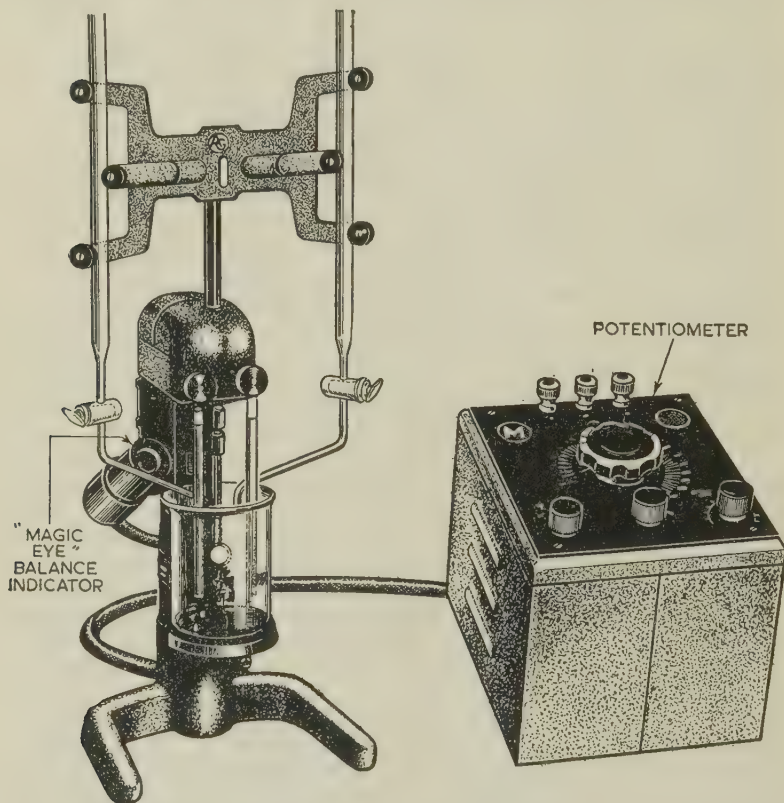
Fig. 12.20. Mullard valve-potentiometer, with "magic-eye" balance indicator. (Courtesy Messrs. Mullard, Ltd., London.)

Fig. 12.21. A sharp, and more or less symmetrical, peak is obtained at the equivalence point. Instead of recording E and v and later computing $\Delta E/\Delta v$ values, one can obtain the differential curve directly, either by using a valve-voltmeter circuit such as that in Fig. 12.19 and balancing out the deflection after each reading, or by a device such as that shown in Fig. 12.22 by means of which the difference between successive E values is read with any type of potentio-

meter. A and B are duplicate electrodes, reversible with respect to the substance in solution which is to be titrated (e.g. Ag electrodes in $AgNO_3$ solution, to be titrated with KCl solution). B is enclosed in a tube which temporarily keeps back a small portion of the solution. Initially, of course, the e.m.f. between A and B is zero, but after a portion of titrant has been added, the e.m.f. of A is thereby changed whereas that of B is un-affected because the solution around B is not mixed with the main bulk. The small e.m.f., ΔE, between A and B is noted, and then the solution is expelled from the enclosure (for example, by compressing a rubber teat attached at the top of the tube). When the compartment refills with solution, the e.m.f., of course, re-

FIG. 12.21. Differential potentio-metric titration graph.

turns to zero and the next addition of titrant can be made. This technique is widely applicable and has the advantages that full sensitivity of the potentiometer or valve voltmeter can be used, and the early stages of the titration can be accomplished rapidly be-cause the approach of the end-point is apparent from the increasing ΔE values.

Examples of potentiometric titra-tions. The following experiments illustrate some of the principal types of titration that can be conveniently carried out potentiometrically. Any of the methods of e.m.f. measure-ment described above can be used if only the equivalence points are re-quired, but a potentiometer accurate to 1 mV should be used if the theory of the titration curves is to be studied in the manner suggested in the text.

FIG. 12.22. Method of carrying out a differential potentiometric titration, using a pair of similar electrodes.

1. *Acid–alkali titrations*. The pH can be determined in the titration with a hydrogen electrode (p. 260), quin-hydrone electrode (p. 269), or glass electrode (p. 271). Some suitable cell assemblies are shown in Figs. 12.13 and 12.23. Many variations are possible[2]; for example, the dipping type of reference electrode shown in Fig. 12.13 (b) can be used with advantage in the other cells provided a valve voltmeter is employed for the e.m.f. measurements.

EXPERIMENTS

Use the hydrogen electrode for the following titrations. (Quin-hydrone or glass electrodes are unsuitable because of the extreme pH values involved.) Titrate (a) 0·1N HCl with 0·1N NaOH, (b) 0·1N acetic acid with 0·1N NaOH, (c) 0·05M H_2CrO_4 or H_3PO_4 with 0·1N NaOH, (d) aniline with acetic acid.

Results. Plot pH against ml of titrant. Note the forms of the curves and the pH at the equivalence points and at the half-neutralization stages. The experiments illustrate the following types of titration curve: (a) strong acid–strong base, (b) weak acid–strong base, (c) dibasic or tribasic acid–strong base (the first stage being a strong acid, the second a weak one and the third, in phosphoric acid, so weak that no inflection point in the curve
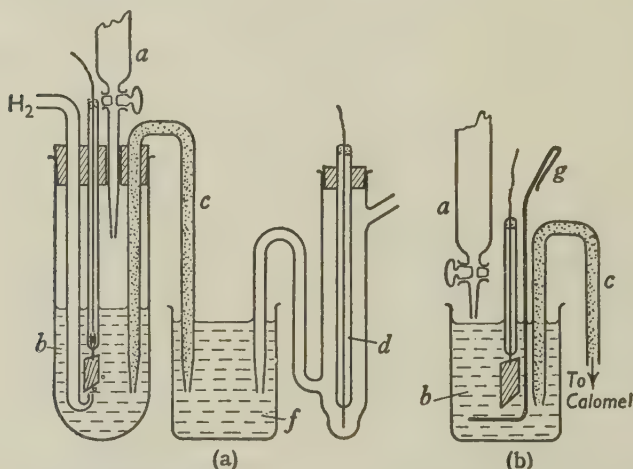
FIG. 12.23. Arrangements for potentiometric titrations with (a) a hydrogen electrode, (b) quinhydrone or other redox electrode.

is seen for Na_3PO_4—i.e. it is largely hydrolyzed into HPO_4^{--} and OH^-), (d) weak base–weak acid (salt almost entirely hydrolyzed).

One may study also the titration of mixtures of weak and strong acids (or bases), and dibasic acids having dissociation constants which do not differ greatly and hence show "overlap" between the first and second stages of neutralization (e.g. oxalic, tartaric, succinic, phthalic acids).

An amphoteric substance like glycine may be titrated with acid and with alkali. At the extremes of pH a correction for the $[OH^-]$ or $[H^+]$ ions in the solution should be applied; a "blank" with an equal volume of pure water is run, and hence the acid or alkali actually *combined* by the substance can be plotted against pH.

EXPERIMENT

Carry out an accurate electrometric titration of a weak acid with a strong alkali, using a quinhydrone or glass electrode, and determine from the results the dissociation constant(s) of the acid. Suitable acids: monobasic—lactic, benzoic, or acetic; dibasic, with groups separated—malonic; dibasic, groups overlapping—tartaric, succinic.

Procedure. Set up a cell as in Fig. 12.23 (b) or 12.13 (a), with a platinum+quinhydrone electrode or glass electrode to measure the pH and a calomel or Ag/AgCl electrode of known e.m.f. (pp. 251, 259) as reference electrode. (In the case of the quinhydrone electrode a preliminary check may be made by measuring the e.m.f. of the cell with $M/20$ potassium hydrogen phthalate in the cell; this should give a pH of 4·00 at 15° C.) To carry out the titrations, place 50 ml of $0.04N$ acid in the titration vessel and titrate it with $0.5N$ NaOH from a 5 ml microburette. The concentration of either the acid or the alkali must be known accurately. The titration should be carried a little past the equivalence point, notwithstanding the reduced accuracy of the electrodes at high pH; the precise pH values are not needed for the calculation, but the inflection point of the titration curve can be judged better if the complete curve is drawn. The complete titration curve should be repeated with a fresh portion of acid as a check on the accuracy.

Calculation

(a) *Monobasic acids.* First locate the equivalence point as accurately as possible by a differential graph of $\Delta E/\Delta v$ or $\Delta pH/\Delta v$ against v (Fig. 12.21). Then compute for a series of points along the titration curve the following quantities: pH, concentration of salt Na^+A^- formed (= concentration of added base = b), concentration of free acid HA remaining (= initial concentration of acid $(a)-b$). According to the elementary theory (neglecting activity coefficients) the dissociation constant of the acid is given by $K_a = [H^+][A^-]/[HA]$. $[H^+]$ is obtained from the measured pH. It derives from the dissociation of the free acid, and therefore $[HA] = a-b-[H^+]$. Also, the concentration of anions, $[A^-]$, derives largely from the acid neutralized (= b) but partly from dissociation of the acid; hence $[A^+] = b+[H^+]$. Therefore $K_a = [H^+](b+[H^+])/(a-b-[H^+])$. This expression may be used to calculate values of K_a for several positions along the titration curve. It can be further simplified if the acid is weak. Then $[H^+]$ is negligible compared with $(a-b)$ or b, and the expression can easily be reduced to $pH = pK_a+\log_{10}[b/(a-b)] = pK_a+\log$ [(ml of titration)/(ml still needed to reach equivalence point)]. A graph of pH against $\log [b/(a-b)]$ should give a straight line of unit slope, and the pH at the point where $(a-b) = b$ (half-neutralization point) gives the pK_a of the acid (= $-\log_{10} K_a$).

Activity correction. The [ ] terms in the above equations ought to be multiplied by their proper activity coefficients. Remembering that pH

can be taken as $-\log a_{H^+}$ (p. 266), the final equation becomes pH $= pK_a' + \log [A^-]/[HA] + \log f_{A^-} - \log f_{HA}$. Provided the solutions are dilute, f_{HA} can be neglected (HA being an uncharged species) and the only correction needed is f_{A^-}. This can be estimated roughly from the simple Debye-Hückel theory (p. 242) as $-\log_{10} f_{A^-} = 0{\cdot}5\sqrt{\mu}$, where μ is the ionic strength of the solution $(= \Sigma\frac{1}{2}c_i z_i^2$, c_i = concn. of typical ion of valency z). (Alternatively, the Güntelberg equation (p. 243) could be used to get a better estimate of f_{A^-}. More refined methods of getting K_a' accurately will be found in textbooks of electrochemistry.) For the present purpose, since only univalent ions are concerned, $\mu = [Na^+A^-] =$ (equivalents of base added)/(vol. of solution in litres). The activity correction need be applied only to the data at the half-neutralization point, as correction of the other points would not alter the result obtained for K_a.

(b) *Dibasic acids*: $K_1 > 100K_2$. For the first dissociation of a dibasic acid, $H_2A \rightleftarrows HA^- + H^+$ and, $K_1 = [H^+][HA^-]/[H_2A]$. The theory is identical with that given for a monobasic acid, and $pK_1 =$ pH of the solution when half an equivalent of alkali has been added. For the second dissociation, $HA^- \rightleftarrows A^{--} + H^+$ and $K_2 = [A^{--}][H^+]/[HA^-]$. If $K_1 > 100K_2$, the first stage is practically complete before the second begins, and the form of the curve between the first and the second equivalents follows the same type of equation as for another monobasic acid. Thus pK_2 can be obtained as the pH of the solution when $1\frac{1}{2}$ equivalents of alkali have been added (i.e. $[A^{--}] = [HA^-]$). In this case the dibasic acid shows two points of inflection, the ml of alkali being in the ratio 1 : 2, corresponding to the formation of NaHA and Na_2A.

(c) *Dibasic acids*: $K_1 < 100K_2$. In this case the titration curve may show no signs of two inflections, only the final Na_2A stage giving a step. This is because the dissociation reactions "overlap", the second starting before the first is nearly complete. If c is the total concentration of acid added to the solution (in mole/litre), and b the concentration of added NaOH, it can be shown by approximate theory similar to that employed above, that for any point on the titration curve the following relationship holds:

$$\frac{b + [H^+]}{[H^+] + 2K_2} = \frac{cK_1}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

In order to get K_1 and K_2 it is necessary to choose two points on the titration curve (say, after $\frac{1}{2}$ and $1\frac{1}{2}$ equivalents of alkali have been added) and solve the resulting pair of simultaneous equations.

It should be added that none of the above equations can be used for strong or for extremely weak acids. For further study of titration curves the reader is referred to monographs on pH.[5]

2. *Precipitation titrations*. Any precipitation reaction can form the basis of a potentiometric titration provided one of the ions can participate in a reversible electrode reaction. However, the reaction may not necessarily provide an accurate analytical method; in some reactions the end-point may be obscured by partial solubility (e.g. $PbCl_2$) or adsorption.

Also, from $\Delta G = \Delta H - T\Delta S$, it follows that $\Delta H = -zEF + TzF(\mathrm{d}E/\mathrm{d}T)$. $(-\Delta H)$ is equal to the heat evolved when the reaction is allowed to proceed unharnessed (e.g. cell short-circuited). $(T\Delta S)$ is equal to the heat absorbed when the reaction is conducted reversibly, as in the balanced cell. As $\mathrm{d}E/\mathrm{d}T$ is usually small, it is necessary to measure E very accurately (say, to ± 0.01 mV) if ΔS and ΔH are to be obtained reliably: consequently, the method is restricted to cell reactions involving the more satisfactory types of electrode.

EXPERIMENT

Determine the equilibrium constant of the reaction $TlCl\ (s) + KSCN\ (aq) = TlSCN\ (s) + KCl\ (aq)$ *by the e.m.f. method and also by analysis. Determine the* ΔS *and* ΔH *values of the reaction.*

Method Set up the following cell.

Tl-amalgam | TlCl(satd.), $0.08M$ KCl || satd. NH_4NO_3 || $0.1M$ KSCN, TlSCN (satd.) | Tl-amalgam

Two half-cells similar to those used for calomel electrodes can be employed, the junction being made by dipping the delivery tubes of both electrode vessels in a tube of satd. NH_4NO_3 solution. All three vessels must be supported in a thermostat. The thallium amalgam, which should be of the same composition in both electrodes, should contain 1–2 per cent of thallium. It is best prepared by electrolyzing a solution of thallium sulphate containing the calculated amount of thallium, with a known weight of mercury as cathode. The e.m.f. of the cell is small; it is determined with an accurate potentiometer, used on its sensitive range, in combination with a sensitive galvanometer or a valve null-point detector. The temperature of the thermostat is changed in steps of $5°$ from $30°$ to $40°$. Sufficient time must be allowed for the cells to reach equilibrium at each temperature.

Equilibrium by chemical analysis. The chemical equilibrium may be determined by shaking, say, 200 ml of $0.1N$ KSCN with 10 g of solid thallium chloride, or 200 ml of $0.1N$ KCl with 10 g of solid thallium thiocyanate. To a portion of the equilibrium solution potassium hydrogen iodate and sulphuric acid are added in order to oxidize the thiocyanic acid to hydrocyanic acid, and the hydrocyanic acid and iodine liberated are driven off by boiling (in a fume cupboard). The chloride remaining is then titrated with silver nitrate.

Another equal portion of the equilibrium solution is titrated with silver nitrate so as to give the total chloride plus thiocyanate. By subtracting from this total the amount of chloride present, one obtains the amount of thiocyanate.

Calculation. When the reaction is allowed to proceed freely (not

where the e.m.f. changes rapidly, and carry the titration well beyond the equivalence point.

Results. Plot the e.m.f. against ml of ceric sulphate (v), and $\Delta E/\Delta v$ against v. Hence deduce the equivalence point, v_0, and calculate the formal redox potential from the e.m.f. of the cell at the point where $v_0/2$ ml. had been added. A graph of e.m.f. versus log [Fe^{+++}]/[Fe^{++}] should give a straight line of slope $2 \cdot 303 RT/F$. Similarly, one can study the cerous–ceric potential in exactly the same way, using the e.m.f. values obtained in the presence of excess ceric sulphate.

BIBLIOGRAPHY 12G: Potentiometric titrations

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[2] See Britton, *Hydrogen Ions*, 3rd edn., 1942 (Chapman and Hall, London); Morton, *J. Pharm. Pharmacol.*, 1952, **4**, 281.
[3] Gay, *Ind. Eng. Chem. (Anal.)*, 1939, **11**, 383.
[4] MacInnes, *op. cit.*, 12A.
[5] See Bibliography 12F.

12H. DETERMINATION OF THERMODYNAMIC QUANTITIES FROM E.M.F. MEASUREMENTS

The e.m.f. of a reversible cell is a direct measure of the maximum available energy (w'_{max}) released by the cell reaction, and this gives at once the Gibbs free energy change (ΔG) of the reaction, i.e. $zEF = w'_{max} = -\Delta G$. Since thermodynamic quantities are usually expressed in calories, zEF (in volts × coulombs = joules) has to be divided by ($J = 4 \cdot 186$ joules/cal). A knowledge of ΔG for the cell reaction makes it possible to calculate the equilibrium constant, K, for the reaction as it would proceed "unharnessed"— for example, if the cell were short-circuited. The relationship is $\Delta G^\circ = -RT \log_e K$; here ΔG° is the *standard* free energy of the reaction, i.e. it is the value of ΔG for the reaction conducted with reactants and products in their standard state (activity = 1). If the cell reaction involves pure solids or gases only, then zEF gives ΔG° directly, but if solutions are involved in the cell reaction, then ΔG° must be calculated from the ΔG value by means of the van't Hoff reaction isotherm, namely, $\Delta G = \Delta G^\circ + RT \log_e X$, where X stands for the mass law product for resultants and reactants at the activities appropriate to the cell. An example of a reaction for which K can be obtained both potentiometrically and by analysis is Tl Cl (s) + KSCN (aq) $\rightleftharpoons$ TlSCN (s) + KCl (aq) (see below).

The *temperature coefficient* of the e.m.f. of a cell provides a method of obtaining the entropy change, ΔS, and heat of reaction. Since $(\partial \Delta G/\partial T)_p = -\Delta S$ and $\Delta G = -zEF$, hence $\Delta S = zF(dE/dT)$.

Also, from $\Delta G = \Delta H - T\Delta S$, it follows that $\Delta H = -zEF + TzF(dE/dT)$. $(-\Delta H)$ is equal to the heat evolved when the reaction is allowed to proceed unharnessed (e.g. cell short-circuited). $(T\Delta S)$ is equal to the heat absorbed when the reaction is conducted reversibly, as in the balanced cell. As dE/dT is usually small, it is necessary to measure E very accurately (say, to ± 0.01 mV) if ΔS and ΔH are to be obtained reliably: consequently, the method is restricted to cell reactions involving the more satisfactory types of electrode.

EXPERIMENT

Determine the equilibrium constant of the reaction TlCl $(s) +$ KSCN $(aq) =$ TlSCN $(s) +$ KCl (aq) *by the e.m.f. method and also by analysis. Determine the ΔS and ΔH values of the reaction.*

Method Set up the following cell.

Tl-amalgam | TlCl(satd.), $0.08M$ KCl || satd. NH_4NO_3 || $0.1M$ KSCN, TlSCN (satd.) | Tl-amalgam

Two half-cells similar to those used for calomel electrodes can be employed, the junction being made by dipping the delivery tubes of both electrode vessels in a tube of satd. NH_4NO_3 solution. All three vessels must be supported in a thermostat. The thallium amalgam, which should be of the same composition in both elec-trodes, should contain 1–2 per cent of thallium. It is best prepared by electrolyzing a solution of thallium sulphate containing the cal-culated amount of thallium, with a known weight of mercury as cathode. The e.m.f. of the cell is small; it is determined with an accurate potentiometer, used on its sensitive range, in combina-tion with a sensitive galvanometer or a valve null-point detector. The temperature of the thermostat is changed in steps of $5°$ from $30°$ to $40°$. Sufficient time must be allowed for the cells to reach equilibrium at each temperature.

Equilibrium by chemical analysis. The chemical equilibrium may be determined by shaking, say, 200 ml of $0.1N$ KSCN with 10 g of solid thallium chloride, or 200 ml of $0.1N$ KCl with 10 g of solid thallium thiocyanate. To a portion of the equilibrium solution potassium hydrogen iodate and sulphuric acid are added in order to oxidize the thiocyanic acid to hydrocyanic acid, and the hydrocyanic acid and iodine liberated are driven off by boiling (in a fume cupboard). The chloride remaining is then titrated with silver nitrate.

Another equal portion of the equilibrium solution is titrated with silver nitrate so as to give the total chloride plus thiocyanate. By subtracting from this total the amount of chloride present, one obtains the amount of thiocyanate.

Calculation. When the reaction is allowed to proceed freely (not

harnessed in a cell), it does so until the constituents reach concentrations satisfying the law of mass action; thus,

$$\frac{a_{TlSCN} \times a_{KCl\ aq}}{a_{TlCl} \times a_{KSCN\ aq}} = K$$

Since TlSCN and TlCl are both present as pure solids in excess, their activities are unity, and hence

$$a_{KCl\ aq}/a_{KSCN\ aq} = K$$

Now $a_{KCl} = a_{K^+}.a_{Cl^-}$ and $a_{KSCN} = a_{K^+}.a_{SCN^-}$, and a_{K^+} is the same for both in an equilibrium mixture: hence $K = a_{Cl^-}/a_{SCN^-}$. The activity coefficients of these ions may be taken as equal, and thus $K = [Cl^-]/[SCN^-]$ (at equilibrium). (K is easily shown to be equal also to the ratio of the solubility products of TlCl and TlSCN.)

If a cell of the kind used above were constructed with KCl and KSCN concentrations such that $a_{Cl^-} = Ka_{SCN^-}$, it would show zero e.m.f. If $a_{Cl^-}/a_{SCN^-} < K$, positive current will flow in the cell from right to left, thereby causing an increase in the concentration of the chloride ion and a decrease in the concentration of the thiocyanate ion. The "driving force" of the cell is then given by

$$\Delta G(= -EF) = -RT \log_e K - RT \log_e a_{Cl^-}/a_{SCN^-}$$

Hence, if E is measured, and a_{Cl^-}/a_{SCN^-} is taken as $[Cl^-]/[SCN^-]$ (used in the cell), then K can be calculated. The value is to be compared with that found by analysis of the equilibrium mixture.

ΔH and ΔS are obtained from dE/dT as explained.

Other reactions suitable for study by the e.m.f. method:

1. The equilibrium constant of the reaction, $Fe^{+++} + Ag \rightleftarrows Fe^{++} + Ag^+$, may be calculated from the e.m.f. of the cell:

$$Pt \left| \begin{array}{l} 0.025M\ Fe(NO_3)_3 \\ 0.075M\ Fe(NO_3)_2 \\ 0.05M\ HNO_3 \end{array} \right| \begin{array}{l} 0.05M \\ HNO_3 \end{array} \left| \begin{array}{l} 0.05M\ AgNO_3 \\ 0.05M\ HNO_3 \end{array} \right| Ag$$

The ferrous nitrate is best obtained by mixing equivalent quantities of $Ba(NO_3)_2$ and $FeSO_4$.

2. The oxidation of hydroquinone by silver ions leading to the equilibrium, $C_6H_4(OH)_2 + 2Ag^+ \rightleftarrows C_6H_4O_2 + 2Ag + 2H^+$, may be studied by means of the cell,

$$Pt\,|\,quinhydrone,\ 0.1M\ HNO_3\,\|\,0.1M\ HNO_3,\ 0.001M\ AgNO_3\,|\,Ag$$
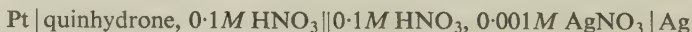
3. For the calculation of heat of reaction from e.m.f., one may study the cell formed by a cadmium (or cadmium amalgam) electrode and a silver–silver chloride electrode immersed in a saturated solution of $CdCl_2$, $2.5H_2O$. The reaction involved is:

$$Cd + 2AgCl + 2.5H_2O = CdCl_2,\ 2.5H_2O + 2Ag$$

It should, however, be remembered that such measurements are of little value unless the e.m.f. can be determined with an accuracy of about 0.01 mV.

4. The free energy, entropy, and heat of the reaction

$$\text{Hg}_2\text{Cl}_2\,(s) + 2\text{KOH}\,(aq) = 2\text{KCl}\,(aq) + \text{H}_2\text{O} + \text{HgO}\,(s) + \text{Hg}\,(l)$$

are obtained from measurements of the following cell:

$$\text{Hg} \mid \text{HgO (satd.)},\ N\,\text{KOH} \parallel \text{KCl (satd.)} \parallel N\,\text{KCl},\ \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$$

If the e.m.f. of the N KCl calomel electrode is assumed (p. 252), the measurements give the free energy, etc., of the reaction

$$\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2\ominus$$

BIBLIOGRAPHY 12H: Determination of thermodynamic quantities from e.m.f. measurements

See monographs cited under 12A and 12E.

12 I.   DETERMINATION OF TRANSPORT NUMBERS FROM E.M.F. MEASUREMENTS

In certain cases cells may be used to obtain transport numbers. This application is based on a comparison of the e.m.f. of concentration cells with and without liquid junctions ("transport"), (cf. p. 245).   Instead of eliminating the junction potential by means of a salt bridge, one can interpose between the two half-cells a metal electrode reversible to the ion of opposite sign to that concerned at the primary electrodes.   For example, the cell

$$\text{H}_2(\text{Pt}) \mid \text{HCl}(a_{\pm})_1 \parallel \text{HCl}(a_{\pm})_2 \mid \text{H}_2(\text{Pt})$$

has an e.m.f. given by $E_1 = 2t_-(RT/F)\log_e (a_{\pm})_1/(a_{\pm})_2$ where t_- is the transport number of the anion.   The double cell

$$\text{H}_2(\text{Pt}) \mid \text{HCl}(a_1),\ \text{AgCl} \mid \text{Ag} \mid \text{AgCl},\ \text{HCl}(a_2) \mid \text{H}_2(\text{Pt})$$
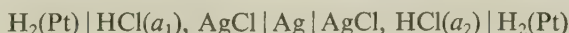
gives

$$
\begin{aligned}
E_2 &= [(RT/F)\log_e (a_{\text{H}^+})_1 - E^\circ_{\text{Ag/AgCl}} + (RT/F)\log_e (a_{\text{Cl}^-})_1] \\
&\quad - [(RT/F)\log_e (a_{\text{H}^+})_2 - E^\circ_{\text{Ag/AgCl}} + (RT/F)\log_e (a_{\text{Cl}^-})_2] = \\
&\frac{RT}{F}\log_e \frac{(a_{\text{H}^+})_1 \cdot (a_{\text{Cl}^-})_1}{(a_{\text{H}^+})_2 \cdot (a_{\text{Cl}^-})_2} = (2RT/F)\log_e (a_{\pm})_1/(a_{\pm})_2
\end{aligned}
$$

Hence the ratio of $E_1/E_2 = t_-$, the transport number of the anion.[1]

EXPERIMENT

Determine the transport number of the lithium ion in lithium chloride.
    The cells required are:
    (1) (with transport) $\text{Ag} \mid \text{AgCl},\ \text{LiCl}(a_1) \parallel \text{LiCl}(a_2),\ \text{AgCl} \mid \text{Ag}$, and
    (2) (without transport) $\text{Ag} \mid \text{AgCl},\ \text{LiCl}(a_1) \mid \text{Li-amalgam} \mid$
        $\text{LiCl}(a_2),\ \text{AgCl} \mid \text{Ag}$

The ratio a_1/a_2 should be about 10 (see Appendix Table A10). The theory,[2] by analogy with that given above, leads to $E_1/E_2 = t_{Li^+}$. The transport number varies a little with the concentrations employed.

BIBLIOGRAPHY 12 I: Determination of transport numbers from e.m.f. measurements

See monographs cited under 12A.

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CHEMICAL KINETICS

13A. INTRODUCTION

A knowledge of thermodynamic quantities such as heats of reaction, free energies, equilibrium constants, etc., enables one to predict the *direction* of a chemical reaction, but gives no information about the *velocity* with which the reaction will take place. Whereas some reactions are practically instantaneous (e.g. reactions between salts in solution), others—particularly in organic chemistry—are normally slow: some potential reactions do not take place at detectable rates unless catalyzed or otherwise initiated (e.g. $2H_2 + O_2 \rightarrow 2H_2O$). A study of the *kinetics* of a reaction (i.e. its rate under various conditions of concentration, temperature, etc.) is usually made in order to elucidate the path or *mechanism* by which it takes place.

Most commonly reactions proceed by steps via intermediate ions, molecules or free radicals, the existence of which is rarely apparent from the stoichiometric equation of the reaction. For this reason the *kinetics* often bear no relation to what might be expected according to the classic ideas of Guldberg and Waage. For example, the rate of the reaction $H_2 + Br_2 \rightarrow 2HBr$ is *not* proportional simply to $[H_2] \times [Br_2]$ but is found experimentally to be proportional to

$$\frac{[H_2] \times \sqrt{[Br_2]}}{\text{const.} + [HBr]/[Br_2]}$$

This expression is consistent with a mechanism involving Br atoms. (For another example, see p. 308.) Similarly, although many gas reactions of the type $A \rightarrow$ products are known, very few are truly *unimolecular*, that is, direct decompositions of single molecules. The great majority of all reactions proceed by one or more *bimolecular* steps despite the molecularity suggested by their equations.

The first step in the empirical study of the kinetics of a reaction (after the stoichiometry and existence or absence of side reactions have been established), is to decide whether it is *homogeneous* or *heterogeneous*, and *catalyzed* or *uncatalyzed*. These factors must be considered in order to get reproducible reaction rates for further study.

The next step is to determine how the rate of the reaction depends on the concentration of reactants (and products, if the

reaction is reversible). If the rate of a reaction $A + B \rightarrow$ products is found to be proportional to $[A]$ it is said to be *first-order* with respect to A. If the rate is proportional to $[A]^x$, it is of xth order with respect to A. If the rate is proportional to $[A]^x[B]^y$, the reaction as a whole is of the $(x+y)^{th}$ order. If the mechanism is simple, x and y will be 0, 1 or 2, but non-integral values merely indicate a complex mechanism (cf. the formation of HBr). If $x = 0$, the *rate-determining step* is independent of the amount of the substance present in the system. Most often $x \approx 1$, and therefore the majority of reactions slow down as the reactants are used up; a few, however, are accelerated by the products of the reaction (autocatalytic). Some proceed by *chain reactions*, which may be *branching*, leading to explosion, or *non-branching* as in most catalyzed polymerization reactions.

All *rate-processes* are accelerated by rise of temperature. The *velocity constant*, k, of the reaction—that is, the specific velocity of the reaction with unit concentration of all reactants—usually follows the Arrhenius equation, $k = Ae^{-E/RT}$, where A and E are practically independent of temperature. E, the *energy of activation* of the process, is interpreted as the minimum thermal energy which the molecules must get before they can undergo reaction. The energy of activation is needed either to break a chemical bond, as in *free radical* gas reactions, or to permit an electronic rearrangement when the reacting molecules collide. In heterogeneous reactions a relatively small activation energy is often found; this generally indicates that the rate of the reaction is controlled by diffusion or other *transport* mechanism rather than by a slow chemical process.

The deduction of the precise molecular mechanism of a reaction from its kinetics often proves a difficult and complex problem; monographs on Chemical Kinetics should be consulted for examples. The present chapter will be confined to experimental methods of studying rates of reaction in order to establish the form of their kinetics under changing conditions.

Methods of measuring rates of reaction. The most convenient reactions to study are those requiring between 1 minute and 1 day to go to completion. The conditions of concentration, temperature, catalysts, etc., must be carefully controlled and known so that a reproducible rate is obtained and the course of the reaction can be quantitatively interpreted.

Innumerable methods have been used for following the progress of reactions. The most obvious one is by chemical analysis; if the reaction can be stopped after a known time by cooling or by addition of some reagent one can analyze the mixture at leisure (see p. 299

for example). The use of a chemical indicator is a special application of the chemical method (example, see p. 308).

It is usually more convenient, however, to use a physical method in order to measure the amount of reaction which has occurred without disturbing the system. Any physical property which changes in a definite manner as the reaction proceeds can be employed as a means of measurement. The following list of examples gives a few of the many properties which have been used; pressure (for gas reactions involving a change in the number of moles of gas—example, see p. 303); volume (gas, p. 302, solution, p. 305); electrical conductivity (p. 303); optical rotation (p. 300), thermal conductivity (gas mixtures); weight (e.g. oxidation of a metal); optical absorption (p. 320); refractive index; pH; viscosity (especially important for polymerization studies).

Form of the kinetics. Since the velocity of a reaction depends on the concentration of reactants, the actual rate in terms of grams of substance reacted in unit time changes during the course of the reaction. The rate can be defined in any convenient way; usually the rate of change of concentration, $[x]$, of one of the reactants or products will be chosen. Thus, the rate of a reaction $A + B \rightarrow C + D$ could be expressed as $-d[A]/dt$, $-d[B]/dt$, $d[C]/dt$ or $d[D]/dt$, and the concentration could be in grams per litre or any other convenient unit. The experimental measurements will show how the concentration of the chosen substance, say x, changes with time, and the rate at any moment is therefore given by the tangent of the $[x]$–t curve.

The chief problem in experimental kinetics is to ascertain how the rate, $d[x]/dt$, depends on the concentrations of the various substances concerned. One method is to vary the concentration of each substance in turn (keeping all other factors constant) and then measure the rate in each instance. Since, however, the rate varies even while the reaction is being studied, it is usually necessary to deduce the order of the reaction from the mathematical form of the $[x]$–t results. The shape of the $[x]$–t curve can readily be predicted for all the simplest types of theoretical reaction mechanism.

Kinetics of 1st-order reactions. By definition, the rate is proportional to the concentration, i.e. $-d[x]/dt \propto [x]$, or $-d[x]/dt = k[x]$, where k, the proportionality constant, is called the *velocity constant of the reaction*; k has the dimensions of time^{-1}.

There are several ways of testing kinetic data for conformity to 1st-order kinetics.

(a) *Tangent method.* Plot a graph of $[x]$ against t. Draw tangents at a number of points along the curve, measure their slopes, and see whether slope/$[x]$ = const. (= k).

(b) *Half-change method.* It is a characteristic of 1st-order kinetics

that the *time of half-change*, that is, the time needed for $[x]$ to fall to half its initial value, is independent of the initial concentration. (The same holds for any other fraction besides $\frac{1}{2}$.) This follows from integration of the defining equation. Separating the variables, one has $d\,[x]/[x] = -k\,dt$. Integrating between (x_1, t_1) and (x_2, t_2) gives $\log_e ([x]_2/[x]_1) = -k(t_2-t_1)$. If $[x]_2 = \frac{1}{2}[x]_1$, $k = \dfrac{2\cdot303}{(t_2-t_1)} \log_{10} 2$. Thus, the interval between t_2 and t_1 should be found constant whatever value of $[x]_1$ is selected on the curve.

(c) *General integral method.* The general integration of the rate equation gives

$$\log_e [x] = -kt + \text{const.}$$

A graph of $\log_{10} [x]$ against t should therefore give a straight line of slope $-k/2\cdot303$. This is the most commonly used method of calculating 1st-order velocity constants, as it makes full use of all the data. It can be applied to any part of the $[x]$–t curve.

(d) *Guggenheim's method.*[1] It sometimes happens that the readings in the middle section of a kinetic determination can be made more accurately than those near the beginning or the end. Method (c) of treating the results gives undue weight to the initial concentration, and this quantity is often not known with as high an absolute accuracy as are the relative differences in the middle of the curve. The following method is then appropriate.

A series of "readings", V (e.g. titrations, value of a physical property, etc.), is made at times $t_1, \ldots t_n$ spread over an interval two or three times the time of half change of the reaction. A second series of "readings" V', is then made at times $(t_1+t') \ldots (t_n+t')$, each exactly at constant interval t' after the corresponding "reading", V. The interval t' should be equal to 2–3 times the time of half-reaction. If the values of $\log_{10} (V'-V)$ are then plotted as ordinates against the times t as abscissae, a straight line is obtained, the slope of which, $\log_{10} (V'-V)/t$, is $-k \cdot \log_{10} e$; or, $2\cdot303 \times \text{slope} = -k$.

The advantage of this method is that the concentration of the reacting substance need not be known at all provided some property "V", which is a linear function of the composition of the system, can be observed.

1st-order kinetics are encountered not only with true unimolecular reactions (which are rare), but also with bimolecular reactions in which the concentration of the second substance is relatively very great ("pseudo-unimolecular reactions", examples pp. 299–304) or is maintained constant (example p. 308). The "decay" of radioactive elements and of the glow of some phosphorescent solids is also 1st-order.

Kinetics of 2nd-order reactions. If the reaction $A + B \rightarrow$ Products is 1st-order with respect to both A and B, the overall kinetics will be 2nd-order. Let the initial concentrations of A and B be a and b respectively, and let the amount of reaction that has occurred after time t be x. Thus, the rate is given by $dx/dt = k(a-x)(b-x)$, where k is the 2nd-order

velocity constant, and has dimensions of concentration^{-1} time^{-1}. Integration of the above equation between 0 and t gives

$$k = \frac{1}{(a-b)t} \log_e \frac{(a-x)b}{(b-x)a} = \frac{2 \cdot 303}{(a-b)t} \log_{10} \frac{(a-x)b}{(b-x)a}$$

When the initial concentrations, a and b, are the same, the corresponding equations are

$$\frac{dx}{dt} = k(a-x)^2, \text{ and } k = \frac{1}{t} \cdot \frac{x}{a(a-x)}.$$

Expressions for the velocity of reactions of a higher order, in which the concentrations of three or more molecular species undergo change, can be obtained in a similar manner. Such reactions are, however, few in number and will not be considered here.

Expressions can also be deduced in a similar way for reversible reactions, free radical and chain reactions.

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13B.   FIRST-ORDER REACTIONS

Only a few gas reactions are true unimolecular decompositions, but numerous examples of reactions which follow 1st-order kinetics are known.

Hydrolysis of an ester, catalyzed by acid. When an ester, such as methyl acetate, reacts with water, it is partially converted into alcohol and acid, according to the equation

$$CH_3.COOCH_3 + H_2O \rightleftharpoons CH_3.COOH + CH_3OH$$
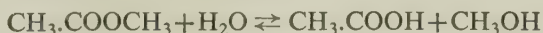
When the amount of water is relatively large, the reaction takes place practically completely as represented, from left to right, and the kinetics are 1st-order. The hydrolysis takes place slowly even with pure water and is catalyzed by acids. The rate is approximately proportional to the concentration, or rather, activity of hydrogen ions.

EXPERIMENT

Determine the velocity constant of the hydrolysis of methyl acetate at 25° C, catalyzed by 0·5N HCl.

Procedure. Prepare a standard solution of baryta, approximately

$N/20$, and determine its titre by means of pure succinic acid, using phenolphthalein as indicator. By means of this baryta solution, prepare also $0.5N$ hydrochloric acid. Clean, steam (p. 206) and dry a 250 ml Pyrex conical flask. Pipette 100 ml of $0.5N$ HCl into it, fit a rubber stopper, and suspend the flask in a thermostat at $25°$ C, with a ring of lead to weight it down. Also suspend in the bath a small stoppered bottle of methyl acetate.

After, say, 10 minutes, when the liquids will have assumed the temperature of the bath, pipette 5 ml of methyl acetate into the flask of acid, shake well, and immediately withdraw 5 ml of the solution. This is allowed to run into 25 ml of ice-cold water in order to arrest the reaction, and the acid titrated as soon as possible by means of the baryta solution. Note the moment, to the nearest second, at which the solution is run into the water; this is taken as the starting-point of the reaction.

About 10 minutes after the first titration, again withdraw 5 ml of the mixture from the flask, and determine the titre as before, noting the moment at which the reaction is arrested. Further titrations are made at successive intervals of, say, 20, 30, 40, 60, 120 minutes. The remainder of the reaction mixture should be left (stoppered) for 48 hours for the reaction to go to completion.

Calculations. The velocity coefficient, k, can be calculated by one or more of the methods given on pp. 297–8. The initial concentration of methyl acetate is proportional to $(T_\infty - T_0)$, where T_∞ is the final titration (HCl+acetic acid) and T_0 is the initial titration (HCl alone). The concentration of methyl acetate at time t is, similarly, $(T_\infty - T_t)$ where T_t is the titre of the sample taken at that time.

Plot a graph of [methyl acetate] (in units of the titre difference) against time, and also of log [methyl acetate] against time. Calculate k in minute^{-1}.

Other experiments. Since the rate of hydrolysis of methyl acetate is proportional to the activity of hydrogen ions, determinations of the velocity constant in the presence of different catalysts may be used to study the degree of dissociation of weak acids, the degree of hydrolysis of salts of weak bases (e.g. urea hydrochloride), the influence of neutral salts on the activity of strong acids, and the general phenomena of acid-base catalysis.[1]

The temperature coefficient of the reaction rate may be determined by repeating the measurements at $30°$, $35°$ and $40°$ C. The experiment described on p. 308, is, however, more convenient for studying the influence of temperature on velocity of reaction.

Velocity of inversion of sucrose. Another acid-catalyzed 1st-order ("pseudo-unimolecular") reaction which has been much studied [2] is the hydrolysis of sucrose into glucose and fructose. The sugars are optically active. Sucrose is dextro-rotatory, while the product ("invert sugar") is laevo-rotatory; hence, during the

reaction the optical rotation changes sign, and the reaction can be followed by means of the polarimeter.

EXPERIMENT

Determine the velocity coefficient of inversion of sucrose by 0·5N hydrochloric acid at 25° C.

Before commencing the experiment, read through the section on polarimetric measurements, Section F.

Procedure. Prepare a solution of cane sugar by dissolving 20 g of pure cane sugar in water and making the volume up to 100 ml, and, if necessary, filter the solution so that it is quite clear. Add a small crystal of mercuric iodide as preservative. Prepare, also, a normal solution of hydrochloric acid. Place 25 ml of the sugar solution and about 30 ml of the acid in separate flasks which have previously been steamed out and dried, and stand them in a thermostat at 25° C.

After having set up the polarimeter and determined the zero, place a jacketed observation tube in the polarimeter, and cause water at 25° C to circulate through the mantle of the observation tube. The circulation of water through the tube must be so regulated that the temperature remains constant to within 0·1° during the whole of the experiment. This should first be tested with the observation tube full of water, in which the bulb of a thermometer is immersed.

The observation tube is dried and replaced in the polarimeter. When the temperature has again become constant, add 25 ml of the acid to the sugar solution, mix quickly, and as soon as possible pour the mixture into the observation tube. Determine the angle of rotation, and note the time at which the reading is made. Preserve a quantity of the mixed sugar and acid solution in a stoppered flask in the thermostat for the final reading of the rotation.

As the angle of rotation alters rather quickly during the first few minutes, a series of five or six readings should be made, one after the other, and the time noted at which the first and last readings are made. The mean value of the angles read, and the middle point of the time period between the first and last readings, should be taken as the initial value of the rotation (A_0) and the starting-point of the reaction, respectively. Further readings, up to the number of eight or ten, of the angle of rotation should be made after periods gradually lengthening from 10 minutes to 2 hours. The observation tube may then be cleaned out and the final rotation determined after at least 48 hours with the solution which had been kept in the thermostat.

Calculation. If A_0 represents the initial angle, and A_∞ the final angle of rotation, after complete inversion has occurred, the initial amount of

cane sugar will be proportional to the total change in rotation, i.e. to $A_0 - A_\infty$. Similarly, at time t_n, if the angle of rotation is A_n, the amount of cane sugar present will be represented by $A_n - A_\infty$. Hence, in accordance with the formula for a unimolecular reaction, one obtains the expression—

$$k = \frac{2\cdot303}{t_n} \left[\log_{10}(A_0 - A_\infty) - \log_{10}(A_n - A_\infty)\right]$$

The angles of rotation must be given their proper sign, rotations to the right being reckoned positive and those to the left negative.

The value of the velocity coefficient should be calculated according to one or other of the expressions given on p. 298.

Decomposition of diazonium salts. In illustration of another method of following the course of a reaction, the decomposition of diazonium salts, e.g. benzene diazonium chloride [3] may be studied. When this salt is warmed with excess of water, it undergoes decomposition according to the equation

$$C_6H_5.N_2Cl + H_2O = C_6H_5OH + HCl + N_2$$

and the course of the decomposition can be followed by measuring from time to time the volume of nitrogen evolved.

Since the concentration of benzene diazonium chloride in the solution is proportional to the total volume of nitrogen which the solution is capable of yielding, the velocity coefficient of the decomposition can be calculated by means of the formula—

$$k = \frac{2\cdot303}{t} \left[\log_{10} V_\infty - \log_{10}(V_\infty - V_n)\right]$$

where V_∞ is the total volume of gas obtained, and V_n the volume of gas collected up to time t_n.

EXPERIMENT

Determine the velocity constant of the decomposition of benzene diazonium chloride.

Procedure. Prepare a solution of benzene diazonium chloride as follows: dissolve 6·64 g of aniline in 21·4 ml of hydrochloric acid (sp. gr. = 1·16); cool in ice-water, and add gradually from a dropping funnel a cold solution of 4·9 g of sodium nitrite in 75 ml of water. After the addition of the sodium nitrite, make the solution up to 1 litre. Place 30–35 ml of this solution in a tube, *A*, of about 3 cm in diameter, into which a side tube, of about 1-mm bore is sealed (Fig. 13.1). The tube, which should be well cleaned and dried before use, should be chosen of such a length that the air-space above the solution is small. The capillary side tube is connected with a Hempel gas burette. The mouth of the tube *A* is

closed by a rubber stopper through which a stirrer, S, passes, and the latter is furnished with a mercury seal, M, to prevent the escape of gas.

In place of a mercury seal, an air-tight gland may be used. (These are made by Messrs. Quickfit and Quartz, Ltd., London.) With these, as with mercury seals, the pressure in the apparatus must be kept close to atmospheric to minimize the chance of leakage. A rather better form of apparatus is a small flask, connected to the gas burette by rubber pressure tubing and immersed in the thermostat and shaken vigorously by a motor-driven eccentric or by a laboratory shaking machine. (The small "Microid" flask-shaker made by Messrs. Griffin and Tatlock, Ltd. (London) is particularly suitable.)

Yet another method of stirring liquid inside a closed apparatus is with a magnetic stirrer. A powerful U-shaped magnet outside the flask is rotated by an electric motor, and causes a piece of iron enclosed inside glass or "Perspex" to revolve inside the flask.

The solution of benzene diazonium chloride having been placed in the tube, the stirrer is inserted, and the apparatus then fitted together, the side tube being connected with the gas burette. The tube with the diazo-solution is immersed up to the level of the stopper in a thermostat, the temperature of which is regulated at about 35°, and the stirrer is set in fairly rapid motion. During this time the tube with the solution should be in open communication with the air, and the gas evolved allowed to escape. After 5–7 minutes, communication with the gas burette is effected while that with the outside air is stopped. The time at which this is done is noted, and this is taken as the starting-point of the reaction. Gas will now collect in the burette, and its volume should be read off at intervals of about 15 minutes. The temperature of the gas and the height of the barometer should also be noted.

Fig. 13.1. Apparatus for determination of the rate of evolution of nitrogen gas from a solution of benzene diazonium chloride.

The end point of the reaction is determined by repeatedly immersing the tube with the reaction mixture in a large beaker of hot water, until, on cooling again to the temperature of the experiment, there is no further increase in the volume of gas evolved.

The velocity constant of the decomposition is then calculated by means of the equation given on p. 302.

Hydrolysis of tertiary amyl iodide. This reaction can be followed conveniently by measurements of electrical conductivity. The hydrolysis is not catalyzed by hydrogen or hydroxyl ions.

The rate-controlling process is probably slow ionization, $C_5H_{11}I \xrightarrow{slow} C_5H_{11}^+ + I^-$, followed by a rapid reaction of the anion with water, $C_5H_{11}^+ + HOH \xrightarrow{fast} C_5H_{11}OH + H^+$. The net chemical change is therefore $C_5H_{11}I + H_2O \rightarrow C_5H_{11}OH + H^+ + I^-$. The conductivity increases owing to the formation of the strong electrolyte, hydrogen iodide.[4]

EXPERIMENT

Determine the order, the velocity constant and the activation energy of the hydrolysis of tertiary-amyl iodide.

Procedure. Place about 50 ml of aqueous alcohol (80% ethanol by volume) in a large, well-corked, boiling tube in a thermostat at 25° C. A second tube containing a dipping-type conductivity cell (p. 206) is placed alongside. When both have had time to take the temperature of the thermostat, pipette about 0·3 ml of tertiary amyl iodide into the solution, stir well with a glass rod, and insert the electrodes. A stop-watch is started and the conductivity measured on any available conductivity bridge—the Mullard "magic eye" bridge is particularly convenient (p. 219). Readings are taken every 30 seconds for 5 minutes, then every minute for 10 minutes. The electrodes are then returned to the empty boiling tube, and the tube containing the reaction mixture is corked and placed in a beaker of water at about 60° for about 5 minutes to complete the hydrolysis. The tube is then cooled, replaced in the thermostat, and the final conductivity is taken when the temperature is 25°.

Other determinations should then be made in the same way, using 0·2 ml and then 0·4 ml of amyl iodide. To ascertain the temperature coefficient of the reaction, determinations can be made at 18°, 30° and 35° C. More frequent readings of conductivity will of course be needed at the higher temperatures.

Results. The conductivity will be approximately proportional to the amount of hydrogen iodide produced. (Alternatively, a calibration curve can be constructed by successively diluting quantitatively the final reaction solution with the 80% ethanol-water solvent and measuring the conductivity at each dilution.) If the conductivity is λ_0 when the stop-watch is started ($t = 0$), λ_t after time t, and λ_∞ at the end of the reaction, the velocity constant for a first-order reaction would be:

$$k = \frac{1}{t} \log_e \frac{(\lambda_\infty - \lambda_0)}{(\lambda_\infty - \lambda_t)}$$

A graph of $\log_{10} \dfrac{(\lambda_\infty - \lambda_0)}{(\lambda_\infty - \lambda_t)}$ against t should therefore give a straight line of slope $k/2\cdot303$. The time of half-change should also be found to be independent of the initial amount of amyl iodide.

The value of k will be independent of the units in which the conductivity is measured, and therefore it is not necessary to know the cell constant of the conductivity cell. Moreover, the results are not affected by traces of electrolyte impurities, since the evaluation of k involves the ratio of two differences.

The energy of activation can be calculated from the values of k at different temperatures by means of the Arrhenius equation (p. 296).

Decomposition of diacetone alcohol.[5] Many reactions in solution can be followed conveniently by noting the small change of volume which occurs during the reaction. Provided the solution is dilute, the volume change is proportional to the amount of reaction that has occurred. The volume change is detected by enclosing a considerable volume of the solution in a vessel having a narrow capillary neck ("dilatometer"). The movement of the meniscus along the capillary can be followed, if necessary, with a cathetometer. The dilatometer method is applicable to many reactions: the chief limitation on its accuracy is set only by the accuracy with which the temperature can be controlled.

A reaction suitable for study by the dilatometer method is the decomposition of diacetone alcohol:

$$(CH_3)_2C(OH).CH_2.CO.CH_3 \rightleftharpoons 2CH_3.CO.CH_3$$

The forward reaction is catalyzed by hydroxyl ions and goes practically to completion in dilute aqueous solution.
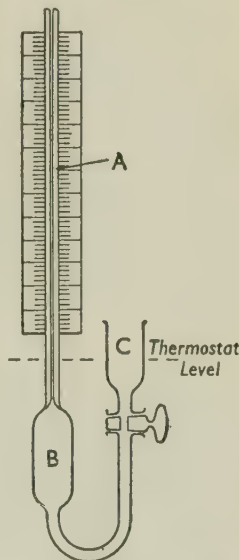
Fig. 13.2. Dilatometer for studying the rate of chemical reactions in solution.

EXPERIMENT

Determine the influence of NaOH *on the rate of decomposition of diacetone alcohol at* $25°$ C.

Apparatus. The dilatometer (Fig. 13.2) consists of a bulb B of capacity about 25 ml, a capillary stem A, a funnel C, and stopcock. The densities of diacetone alcohol and acetone are 0·931 and 0·788 respectively; consequently one may anticipate that 25 ml of a 5% solution would expand by about 0·17 ml during the reaction. This corresponds to a movement of about 20 cm in a capillary 1 mm bore, and can therefore be measured by means of a scale of glass or stainless steel laid along the capillary. Alternatively, of course, a cathetometer may be used.

A simple calculation shows that *it is essential to use a thermostat capable of controlling the temperature to within* $0·01°$ (see Ch. 3B).

Procedure. Clean and dry the dilatometer, and fasten it in a thermostat so that all the bulb is immersed. Pipette exactly 35 ml of $N/10$ NaOH into a small flask, and leave it in the thermostat for 10 minutes. Then add 2·0 ml of diacetone alcohol from a pipette, mix well, and carefully pour the solution into the funnel C of the dilatometer. Open the tap and by means of suction at A adjust the level of the meniscus in the capillary until it stands near the bottom of the scale. Then close the tap. The dilatometer must, of course, be free from air bubbles.

This experiment is most conveniently treated by Guggenheim's method of calculation (p. 298), as it is then unnecessary to know either the initial or final volumes. Accordingly, readings are taken of the position of the meniscus every 5 minutes for a period of about 45 minutes, and a second set of readings is taken (also at 5-minute intervals) after the expiry of one hour from the start.

The experiment should be repeated with several different concentrations of NaOH, e.g. $N/2$, $N/5$, $N/20$. In these cases the time intervals between readings must be modified according to the velocity of reaction; but in every case the interval between the two sets of readings should be greater than $t_\frac{1}{2}$, the time of half-change of the reaction. As a rough guide it may be taken that

$$t_\frac{1}{2}\ (\text{mins}) \times [\text{OH}^-](\text{mole/litre}) \approx 5$$

Calculation. Use Guggenheim's method (p. 298) to evaluate the 1st-order velocity constant of the reaction at each concentration of NaOH. The change of volume may be assumed proportional to the amount of reaction. The results consist of a set of readings $r_1, r_2, r_3 \ldots$ taken at times $t_1, t_2, t_3 \ldots$, and a second set, $r_1', r_2', r_3' \ldots$ taken at (t_1+T), (t_2+T), $(t_3+T) \ldots$ where T is the interval of time between the beginnings of the first and second sets of readings. For the nth readings of each set, the theory gives,

$$2 \cdot 303 \log_{10} (r_n' - r_n) = \text{const.} - kt_n$$

A graph of $\log (r_n' - r_n)$ against t_n therefore gives a straight line of slope $-k/2 \cdot 303$.

Evaluate k for each concentration of NaOH and note the relation between these quantities.

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13C. SECOND-ORDER REACTIONS

Most gas reactions occur by bimolecular processes, and many reactions in solution follow 2nd-order kinetics, although their mechanisms may not necessarily be simple bimolecular ones.

Hydrolysis of esters by alkalis. Many hydrolytic reactions are catalyzed by alkalis as well as by acids, but the overall kinetics are now 2nd-order instead of 1st-order because, with alkalis, the catalyst is consumed in the reaction:

$$R.COOR' + OH^- \to R.COO^- + R'OH$$

The reaction can be followed by titration of the alkali remaining in solution, or, better, by measurements of the electrical conductivity.[1] The net result of the reaction, as regards the conductivity, is that OH^- ions are progressively replaced by $R.COO^-$ ions. The latter have a lower electrical mobility (e.g. the mobility of CH_3COO^- is about one-fifth of that of OH^-); consequently, the conductivity falls. The change of conductivity is approximately proportional to the amount of reaction that has taken place.

EXPERIMENT

Determine the 2nd-order velocity constant of the hydrolysis of ethyl acetate by sodium hydroxide.

Method (a)—Titration. The technique is similar to that used for the acid hydrolysis of methyl acetate, but the reaction occurs more rapidly. Mix 50 ml of $M/60$ solution of ethyl acetate and 50 ml of $N/40$ NaOH (carbonate-free) at $25°$ C. Take 10 ml samples after 3, 5, 10, 20, etc., minutes, running them into 10 ml of $N/20$ HCl to stop the reaction. Titrate the excess acid with baryta. The final titration is made after 24 hours. The velocity constant is calculated by the formula given on p. 299. The terms in the logarithm can be replaced by the number of ml of acid required to neutralize the alkali in the reaction mixture at the beginning (T_0), after time t minutes (T_t), and at the end of the reaction (T_∞), but the term ($a-b$) in front of the logarithm must be expressed in g equiv. per litre. Thus,

$$k = \frac{2 \cdot 303}{([\text{NaOH}]_0 - [\text{EtAc}]_0)t} \cdot \log_{10} \frac{T_t(T_0 - T_\infty)}{T_0(T_t - T_\infty)}$$

Method (b)—Conductivity. The following solutions are required: 100 ml $N/20$ NaOH, 50 ml $N/5$ ethyl acetate, and 100 ml $N/100$ sodium acetate, made by neutralizing 20 ml of the $N/20$ NaOH with acetic acid and making up to 100 ml. All the solutions should be prepared with CO_2-free water.

The reaction is carried out in a solution which is initially $N/100$ with respect to both ethyl acetate and NaOH. The conductivity at

the beginning will thus be that of $N/100$ NaOH, while at the end it will be that of $N/100$ sodium acetate. It is convenient to find these initial and final values of the conductivity before following the course of the reaction.

A conductivity cell having electrodes of about 1 sq. cm, separated by 1–2 cm, is suitable. Any type of conductivity bridge can be used, but the commercial "magic eye" type is particularly convenient as readings can be taken very rapidly. (See Ch. 10 for the technique of conductivity measurements.)

Procedure. First measure the cell resistance with (a) $N/100$ NaOH ($= R_0$) and then (b) $N/100$ CH$_3$COONa ($= R_\infty$) at 25° C.

Now suspend two flasks in the thermostat, one containing 20 ml $N/20$ NaOH + 50 ml CO$_2$-free water and the other 5 ml $N/5$ CH$_3$COOEt + 25 ml of CO$_2$-free water. While they are taking the temperature of the bath (10 minutes) clean and dry the conductivity cell. Then mix the two solutions thoroughly and quickly, and start a clock. Fill the cell with the mixture and take readings of its resistance at frequent, timed intervals as long as the reaction is still occurring.

Calculation. The 2nd-order rate expression for a reaction in which the two reactants are at equal concentration, a, is $k = \dfrac{1}{t} \cdot \dfrac{x}{a(a-x)}$. In this experiment $a = 0 \cdot 01$ g equiv./litre. The amount of reaction that has occurred, x, and the amount of reactants remaining, $(a-x)$, can be deduced from the conductances (C). These are calculated as reciprocals of the cell resistances; thus, initially $C_0 = 1/R_0$; after time t minutes $C_t = 1/R_t$, and finally $C_\infty = 1/R_\infty$. The total amount of reaction possible is proportional to the total change of conductivity, i.e. $a \propto (C_0 - C_\infty)$. Therefore the amount of reaction after time, t, namely, x, is proportional to $(C_0 - C_t)$. Substituting in the above expression, one finds

$$k = \frac{1}{0 \cdot 01 t} \cdot \frac{C_0 - C_t}{C_t - C_\infty}$$

A graph of $(C_0 - C_t)/(C_t - C_\infty)$ against t should therefore give a straight line of slope $0 \cdot 01 \, k$. The units of k are (g equiv./litre)$^{-1}$ min^{-1}.

The reaction H$_2$O$_2$ + 2HI → I$_2$ + 2H$_2$O. This reaction is kinetically of 2nd-order—not, as might be expected, 3rd-order. The mechanism is probably an initial, rate-determining step according to the equation H$_2$O$_2$ + I$^-$ → H$_2$O + IO$^-$ (slow), followed by a rapid reaction given by IO$^-$ + 2H$^+$ + I$^-$ → H$_2$O + I$_2$ (fast). (The latter presumably also occurs by steps, not by a simultaneous collision of four ions!)

The order of the reaction *with respect to H$_2$O$_2$* can be studied conveniently by choosing conditions such that there is practically constant excess of HI. The kinetics then follow the 1st-order law. Experimentally, this is achieved by continually adding small volumes of sodium thiosulphate solution to remove the iodine as soon as it is liberated and to regenerate iodide according to the reaction

$2Na_2S_2O_3+I_2 = Na_2S_4O_6+2NaI$. By using a large volume of solution and adding small amounts of *concentrated* thiosulphate solution from a microburette, one can neglect the small increase of volume of the solution and take the concentration of I^- ions as constant. The rate of the reaction then depends only on $[H_2O_2]$ and temperature. The course of the reaction can readily be followed by timing the appearance of iodine (indicated by starch solution) after a small, known volume of thiosulphate solution has been added. Another addition of thiosulphate is made immediately the blue colour reappears.

The order of the reaction with *respect to HI* can be determined by determining the 1st-order velocity constant of the reaction with different concentrations of HI.

EXPERIMENT

Study the kinetics of the reaction between H_2O_2 and HI.

Procedure. Dissolve *exactly* 2 g of KI in 500 ml of water in a flask (preferably the "bolthead" type). Add 25 ml of dilute H_2SO_4 (1 vol. conc. H_2SO_4 mixed with 2 vols. of water) and 10 ml of starch solution. Arrange the flask so that it is deeply immersed in a bath of ice and water. While the solution is cooling, prepare an approximately "2-volume" solution of H_2O_2 and standardize it by the following method:

Dilute 20 ml of the sulphuric acid to 100 ml, add about 2 g of KI, warm to 30°, and add 10 ml of the H_2O_2 solution. Mix, and allow to stand for 10 minutes. Titrate the iodine liberated with N-$Na_2S_2O_3$, using a microburette.

Arrange a microburette filled with N $Na_2S_2O_3$ over the flask in the bath so that it will deliver directly into the solution. It is convenient to attach to the bottom of the burette a bent tube with a narrow jet, so that the burette need not be vertically above the neck of the flask; this leaves room for a small electric motor and glass stirrer. The speed of the motor should be set at a suitable value by means of a rheostat. Rapid mixing is needed.

Set a stop-clock to zero. Take the temperature of the solution in the flask. Pipette in 25 ml of the H_2O_2 solution, and start the clock when the pipette is half discharged into the flask. Immediately run in 0·3 ml of the $Na_2S_2O_3$ solution from the burette so that the blue colour initially formed is discharged. Observe the solution closely and when the blue colour reappears note the time (without stopping the clock), and immediately run in 0·2 ml of thiosulphate. Again time the reappearance of the blue colour.

Continue in this way until the reaction has reached about half its theoretical course. It is the reappearance of the blue colour

that must be timed—not the addition of thiosulphate. The addition should, however, be made with as little delay as possible. At the end of the readings take the temperature of the solution again, and assume a mean value for the temperature of the experiment.

To determine the temperature coefficient of the reaction, repeat the experiment at 10° and 20° C. Initial additions of 0·5 ml and 1·0 ml of thiosulphate solution, followed by 0·3 ml and 0·5 ml additions will be found suitable at the respective temperatures.

To determine the order of the reaction with respect to HI, the experiment may be repeated at any one temperature (say 10°, for convenient rates) with half and double the amounts of KI and H_2SO_4 in the same total volume of reaction mixture.

Results. The experimental data obtained correspond to the amount of iodine which has been liberated by the reaction (measured in terms of equivalent ml of $Na_2S_2O_3$ solution) at a series of times (as noted from the clock). The total amount of iodine which would be liberated in infinite time is also known—from the preliminary standardization. Since 1 molecule of H_2O_2 is destroyed for every molecule of I_2 liberated, the results provide values of the term $[H_2O_2]$ as a function of time and permit calculation of the 1st-order velocity constant for the rate of reaction of H_2O_2 at constant concentration of iodide, i.e. $-d[H_2O_2]/dt = k_1[H_2O_2]$. The data obtained from the experiment at 0° should be treated by methods (a), (b), and (c) for 1st-order reactions (pp. 297–8). Method (c) will be found the most convenient, and should be adopted for all the other experiments.

In order to calculate the *energy of activation* of the reaction, the Arrhenius equation (p. 296) is put in the form $2·303 \log_{10} k_1 = \log_e A - E/RT$. Since $\log_e A$ is constant, a graph of values of $\log_{10} k_1$ against $1/T(°\,\mathrm{K})$ is therefore a straight line. The slope of the line is equal to $-E/(2·303R)$. If R is taken as 1·99 cal mole^{-1} degree^{-1}, the units of E are cal mole^{-1}.

The order of the reaction with respect to HI can be observed from the effect of [HI] on k_1 (at const. temp.). The 2nd-order velocity constant for the overall reaction is given by $-d[H_2O_2]/dt = k_2[H_2O_2][HI]$. Therefore $k_2 = k_1/[HI]$. If experiments are done with several values of [HI], the same value of k_2 should be obtained (at any one temperature).

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13D. HETEROGENEOUS REACTIONS

All the reactions considered so far are homogeneous reactions in solution, and their velocities are generally governed by the rate of collision of the reacting species. Another class of reactions comprises those in which substances present in different phases participate—heterogeneous reactions.

In industrial chemistry heterogeneous reactions are more important than homogeneous reactions.   Consider, for example, the large-scale reactions concerned in the extraction and refining of metals, the production of water-gas, the softening of water, dyeing of textiles, catalytic hydrogenation of oils, and catalytic synthesis of SO_3, NH_3, CH_3OH, etc.   In such processes the rate is rarely controlled by slowness of chemical reaction ; it is usually limited either by the rate at which the reacting substances can be brought together ("transport-controlled reactions")[1] or by factors concerned with adsorption or desorption of substances on a catalytic surface. These factors are illustrated by the following experiments.

Reactions of ion-exchange resins. Modern ion-exchange resins (as used in water softening, etc.) consist of insoluble granules of a polymerized, cross-linked acid or base. An important type of "strong-acid resin", for example, is composed of insoluble sulphonated polystyrene.   All the sulphonic acid groups in the material are able to react with alkali to form stoichiometric salts, but in contrast to homogeneous ionic reactions, which are practically instantaneous, the rate of the reaction $H^+R^- + M^+OH^- \rightarrow M^+R^- + H_2O$ (where R^- stands for the resin substance and M^+ is a metal ion) is controlled by transport of MOH from the solution to the surface of the particle and into the interior of the particle.[2]   The rate of reaction is therefore affected by the rate of stirring of the solution, the particle size of the resin grains, the concentration of the solution and by the temperature (in so far as it changes the rate of diffusion in the solution or inside the resin).

Under some conditions, the chief resistance to reaction lies in the transport of substance through the solution to the particles.   Improved stirring then increases the rate by bringing fresh solute close to the surface.   However, perfect transport cannot be achieved because the layer of liquid in contact with the solid surface is necessarily stationary.   There is therefore a more-or-less stagnant film of liquid round the particles, and the only mechanism of transport through this film is *diffusion*, a relatively slow process.   Nernst (1904) proposed that the kinetics of such heterogeneous processes could be represented by an expression of the type $dx/dt = AD \cdot \Delta C/\delta$, where A is the area of the interface, D the diffusion coefficient of the substance diffusing, ΔC the difference between the concentration of the substance at the surface and in the bulk of the solution, and δ is the effective thickness of the unmixed layer of solution ("Nernst film").   The thickness, δ, depends only on hydrodynamic factors such as the stirring.

Under other conditions (efficient stirring, high concentration in solution, large ions) the rate of transport in the solution may become

more rapid than transport within the particle; diffusion inside the resin then becomes the rate-determining factor.

EXPERIMENT

Study the kinetics of reactions with a sulphonic acid ion-exchange resin.

Materials. "Zeo-Karb 225" (Permutit Co., Ltd., London) or "Dowex 50" (Dow Chemical Co., Midland, U.S.A.) are suitable. These materials are supplied in the form of spherical grains, produced by suspension-polymerization. If possible, samples of two or more different grain-sizes should be used (e.g. coarse, 20–30 mesh, medium 50—100 mesh, fine 100–200 mesh sieve).

To prepare the resins in the acid form, they should first be treated in a column with portions of $2N$ HCl amounting in all to a considerable excess over the stoichiometric quantity. (The equivalent weight of the dried resin is about 200; the air-dried form has also about 40% water.) The resin is then washed thoroughly until the effluent is free from acidity; it is dried on filter-paper, and then overnight in the air. The resin should then be well mixed and stored in a stoppered bottle so that the moisture content remains constant.

Procedure. Weigh 0·5 g of resin into a beaker containing 100 ml of water and 3 drops of bromo-cresol green indicator solution. Into a second beaker pipette 10 ml of $N/10$ KCl and 100 ml of water. Arrange a stirrer, driven by an electric motor, to agitate the resin suspension vigorously, and also set up a burette containing $N/5$ KOH solution to deliver into the same beaker.

To start the exchange reaction, pour the contents of the second beaker into the first, start a clock, and quickly run in 1 ml of KOH from the burette. When the indicator changes back again to the acid form, note the time, and add a further 1 ml of KOH. Continue in this way, adding 1 ml portions of KOH and noting the time at which it is neutralized, until the reaction becomes too slow for convenient observation. Then stop the stirrer, allow the resin to settle, and tip a little solid KCl on to it in order to displace any remaining acidity still present in the resin. Allow the beaker and contents to stand for about a quarter of an hour, and then titrate the contents with the same burette of KOH until the equivalence point of the indicator is just reached. The final burette reading gives the total exchange capacity of the sample of resin (V_∞), while the intermediate volume readings (V_t) give the amount of exchange which has occurred at a series of times, t. It should be noticed that the concentration of KCl remains practically constant during the experiment.

The instructions given above apply to an experiment in which 20–30 mesh resin is used. With more finely-divided resin the reaction is faster, and it may be necessary to add larger portions of KOH or use smaller amounts of resin or greater volumes of more dilute KCl solution in order to obtain a convenient reaction velocity. A few preliminary experiments may be needed to find suitable conditions.

The determination should be repeated with several different quantities of KCl in the solution, using, of course, fresh portions of resin for each experiment. If the effect of particle size of the resin is to be studied, the mean surface area of each batch should be estimated from microscopical examination or sedimentation experiments.

Treatment of results. The form of the kinetics is seen by plotting a graph of V_t/V_∞ (= F) against t. It will be found that the kinetics do not fit to the 1st- or 2nd-order equations. Instead, the kinetics are determined by diffusion of ions through the boundary film of liquid which surrounds the particles.[2]

Let δ be the effective thickness of the unmixed Nernst film; A the surface area of the resin; D_H and D_K the diffusion coefficients of H^+ and K^+ ions respectively through the solution; $[H^+]_s$ and $[K^+]_s$ the concentrations of these ions in the mixed solution; $[H^+]_r$ and $[K^+]_r$ their concentrations next to the resin surface; K the approximate mass action equilibrium constant for the ion exchange reaction, defined by equation (3) below. Q_t is the amount of exchange in g equiv. that has occurred in time t.

The following equations must hold according to Fick's law of diffusion: for diffusion of the K^+ ions from the solution towards the resin

$$\frac{dQ_t}{dt} = \frac{AD_K}{\delta}([K^+]_s - [K^+]_r) \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

For the diffusion of H^+ outwards from the resin through the Nernst film

$$\frac{dQ_t}{dt} = \frac{AD_H}{\delta}([H^+]_r - [H^+]_s) \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

As the solution is kept alkaline during the experiment, $[H^+]_s$ is negligible in this equation.

Thirdly, the assumption can be made that the electrolyte solution in immediate contact with the resin surface is in exchange equilibrium with the resin; consequently,

$$\frac{[H^+]_r \times [K \text{ resin}]}{[K^+]_r \times [H \text{ resin}]} = K \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

Putting $\dfrac{[K \text{ resin}]}{[H \text{ resin}]} = \dfrac{Q_t}{(Q_\infty - Q_t)}$, it becomes possible to solve the three

simultaneous equations, eliminating the unknown quantities $[H^+]_r$ and $[K^+]_r$. The resulting differential equation is

$$\frac{dQ_t}{dt}\left[1+\frac{D_K}{KD_H}\left(\frac{Q_t}{Q_\infty-Q_t}\right)\right]=\frac{AD_K[K^+]_s}{\delta}$$

On integration, this finally gives a kinetic equation of the form

$$\frac{Q_\infty}{Q_i}\log_e\left(\frac{Q}{Q_\infty-Q_t}\right)=\frac{AKD_H[K^+]_s}{\delta}\left(\frac{t}{Q_t}\right)+\left(1-\frac{KD_H}{D_K}\right)$$

or

$$-\frac{1}{F}\log_e(1-F)=\frac{AKD_H}{\delta}\cdot\frac{[K^+]_s}{Q_\infty}\left(\frac{t}{F}\right)+\left(1-\frac{KD_H}{D_K}\right)$$

The experimental data can be tested for conformity to this mechanism by plotting graphs of $(1/F)\log(1-F)$ against (t/F). These should be straight lines of slope proportional to the $[K^+]_s$ used in the experiment, and they should have the same intercept on the ordinate axis. The slopes of the lines should be proportional to the surface area of the resin used.

When similar experiments are conducted with more concentrated solutions of KCl, it is found that the kinetics follow a different form. This is now consistent with a mechanism controlled by diffusion within the resin grains.[2]

Decomposition of ammonia. Just as the reaction $N_2+3H_2\rightarrow2NH_3$ proceeds most readily in the presence of certain solid catalysts, so the decomposition of gaseous ammonia occurs more rapidly as a heterogeneous reaction on the surface of catalysts such as tungsten than as a homogeneous reaction.[3] Since the decomposition is accompanied by a doubling of the number of molecules, it can readily be followed by the increase of pressure in a constant volume apparatus. The increase of pressure is then proportional to the amount of ammonia decomposed.

The heterogeneous reaction can be studied conveniently by employing an electrically heated tungsten wire as the catalyst. The temperature of the tungsten can be controlled by adjusting the current supplied to the wire. The temperature-dependence of the resistivity R, in ohm-cm of tungsten is given below.[4]

Temp. (° K)	900	1,000	1,100	1,200	1,300	1,400	1,500	1,600	1,700
$R(\times10^{-6})$ (ohm-cm)	21·94	24·90	28·10	31·06	34·10	37·18	40·38	43·50	46·78

A given temperature can therefore be obtained by adjusting the current to produce the required resistance.

The rate of a surface reaction may be dependent on (a) the rate

at which molecules of reactant are adsorbed on the surface, (b) the rate at which reaction of the adsorbed molecules takes place, or (c) the rate at which the products are desorbed, leaving vacant sites on the surface for further reaction. In the present reaction it is found that the reaction is of zero-order, i.e. the rate is independent of the ammonia pressure, except at low pressures (where the rate begins to fall off). This is taken to indicate that the surface is practically covered with adsorbed ammonia at all ordinary pressures. The rate-controlling process is thought to be the desorption of N_2 molecules from the surface. The evidence for this theory lies largely in the fact that on several catalysts the activation energy for ammonia
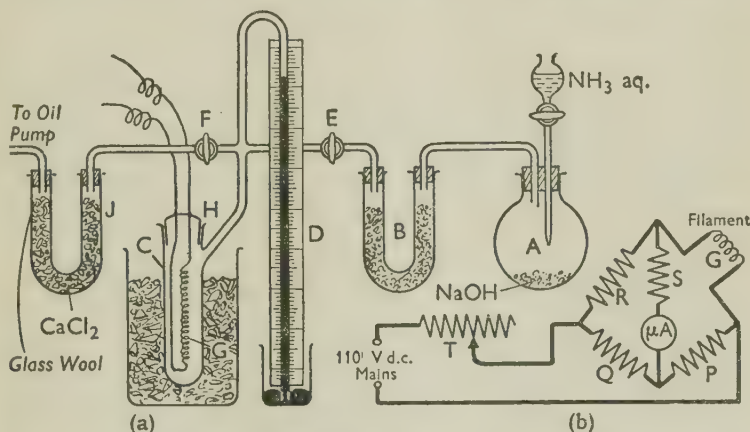
Fig. 13.3. Apparatus for determining the rate of decomposition of ammonia gas by a tungsten filament.
(a) Vacuum apparatus. (b) Electrical circuit.

decomposition is of the same order as that for the desorption of chemisorbed nitrogen.

EXPERIMENT

Determine the order of reaction and the activation energy of the heterogeneous decomposition of ammonia.

Apparatus. The glass and electrical apparatus is shown in Fig. 13.3. Ammonia gas is produced by dropping fresh 0·880-ammonia solution on to solid NaOH in a flask A; it is dried by passage over more NaOH in a U-tube B and is then admitted to the reaction bulb C and manometer D. This part of the apparatus can be isolated by stopcocks E and F; it is preferably made of Pyrex glass. The U-tube J contains calcium chloride and glass wool to protect the rotary oil vacuum pump from moisture and dust.

The tungsten filament G consists of 30·0 cm of 0·1 mm diameter wire, and is attached to stout tungsten leads which are sealed through the removable Pyrex stopper H. In order to control the temperature of the filament, the current passed through it can be adjusted by a rheostat T, in series with the 110 V d.c. mains. Owing to the production of hydrogen during the reaction, the thermal conductivity of the gas will rise and the temperature will tend to fall. This must be counteracted by increasing the current so as to keep the *resistance* of the filament constant. The filament G is therefore connected into a Wheatstone bridge circuit $GPQR$ (Fig. 13.3 (b)), the balance of which is indicated on a centre-zero needle galvanometer or micro-ammeter protected by a resistance S of say 10,000–50,000 ohms. Resistance R is 15·3 ohms, made from nichrome wire. Arms P and Q of the bridge are provided by a Post Office box. Q is set at 1,000 ohms, and several values of P are employed in successive experiments to obtain different filament temperatures: 750, 800, 850 and 900 ohms are suitable values of P. *The current must not be switched on while the apparatus contains air, as the filament will burn out immediately. Also, the reaction vessel must be kept cool by an ice bath.*

Procedure. Place about 5 g of sodium hydroxide pellets in the 250 ml round-bottomed flask A, and about 10 ml of fresh 0·880-ammonia in the tap-funnel. Start the pump with all taps closed and then carefully open first tap F and then tap E. Then close tap F and see if the apparatus is vacuum-tight by watching the manometer for a few minutes. If there is no leakage, run in ammonia solution *drop by drop* from the tap funnel. When a pressure of about 40 cm is shown by the manometer close tap E and pump out the gas by opening F. After evacuation close tap F and admit 20 cm of ammonia by carefully opening tap E. A beaker of ice-water is placed around the reaction bulb and well stirred. After about 10 minutes the manometer is read, giving the initial pressure of gas at 0° C.

For the first determination set resistance P at 850 ohms. Immediately the current is switched on, the rheostat T must be quickly adjusted so that the galvanometer needle returns to zero, and throughout the experiment T must be continually adjusted to maintain zero deflection. A stop-watch is started immediately the current is switched on. After about 30 seconds, during which the rheostat is constantly adjusted, the current is switched off. The ice-bath is stirred, and the manometer tapped until the mercury level reaches a constant position. The pressure reading is then taken, the gas being at 0° C. The current is switched on again and the procedure repeated at convenient time intervals. After sufficient readings have been obtained, the remaining ammonia is decom-

posed by heating the wire to dull red heat for a minute or two. This should be repeated to make sure that decomposition is complete.

The whole experiment should be repeated once with the same resistances and same initial pressure of ammonia and then with 750, 800, and 900 ohms for P in place of 850 ohms.

Calculations. For each series of measurements calculate the temperature of the filament from its dimensions, resistance and resistivity. For each temperature plot a graph of the amount of ammonia decomposed against time, and deduce the initial rate of reaction at 200 mm pressure. The activation energy for the heterogeneous reaction can be calculated by applying the Arrhenius equation in the normal way, i.e. a graph of $\log_e$ (rate) against $1/T$ should give a straight line, the slope of which is equal to $-E/R$ (p. 296).

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13E. PHOTOCHEMICAL REACTIONS

Many reactions, some of which do not proceed under ordinary conditions, take place if the reactants are irradiated with visible or ultra-violet light. The light may serve merely as catalyst to initiate a spontaneous reaction (e.g. $H_2 + Cl_2 \rightarrow 2HCl$) or it may provide the necessary free energy for a reaction which is otherwise thermodynamically impossible (e.g. $CO_2 + H_2O \rightarrow$ carbohydrates, in photosynthesis). In either case the light must be *absorbed* to have any effect. This produces *electronic excitation* in the absorbing atoms or molecules. Since light consists of quanta, the extra energy thus introduced into individual molecules is given by $h\nu$ (h = Planck's constant, ν = frequency of absorbed light), and calculation shows that $h\nu$ is large compared with thermal energies and often great enough to break chemical bonds. Many photochemical gas reactions do, in fact, proceed by way of dissociation of molecules into atoms (e.g. $Cl_2 \overset{h\nu}{\rightarrow} 2Cl$). In other cases excitation provides energy of activation for a reaction, without intermediate dissociation (e.g. in the photo-dimerization of anthracene). The shorter the wavelength, the more powerful the light.

Absorption of light does not necessarily lead to reaction. The excited molecule may re-emit light energy (*fluorescence*), or the energy may be degraded to heat, or it may release electrons (*photo-emission*

effect and *photoconductivity*). Consequently, although the *primary process* (absorption of light) in photochemistry is always at the rate of 1 molecule (or atom) excited per quantum absorbed, the *secondary process* (i.e. subsequent reactions, etc.) may not show any such equivalence. The *quantum yield* is the number of molecules reacting per quantum of light absorbed; it may be less than unity (for reasons indicated) or greater—namely, when the light starts a spontaneous chain reaction.

In some cases reactions can be made to proceed with light of a wavelength which is not absorbed by any of the reactants; the absorption can be effected by another substance which can transmit the absorbed energy to the reactants and itself remain unchanged. This is *photosensitization*, (e.g. photosensitization of the decomposition of oxalic acid in near ultra-violet light by addition of uranyl salts). In some systems thermal reactions proceed simultaneously with photochemical ones, and may enhance or reverse the effect of light. In the latter case a *photo-stationary state* may be set up, as, for example, in the experiment described on p. 319.

The technique of research in photochemistry is somewhat specialized. Powerful mercury arc lamps are the favourite source of illumination since one can obtain a high intensity of monochromatic light of various wavelengths by use of filters or monochromator (Ch. 8). Determination of the absorption spectra is essential, since one must identify the initial step in the process. The stoichiometric equation of the reaction must be established. Some physical or chemical means must be found for determining the amount of reaction which takes place during irradiation. The other principal problem is measurement of the amount of light which has been supplied, so that the quantum efficiency of the reaction can be evaluated. Light intensities are generally measured in photochemistry by means of multiple-junction thermopiles which are previously calibrated in absolute units by means of standard tungsten filament lamps. Thermopiles measure total radiant energy and are therefore not selective, whereas photocells have high spectral selectivity (p.p 165, 167). Quartz apparatus must be used for work in the ultra-violet since light of wavelength less than about 3,500 Å is strongly absorbed by ordinary glass.

Another method of measuring high light intensities for photochemistry in the ultra-violet is by means of a chemical "actinometer" reaction, the quantum efficiency of which has been previously determined by the absolute physical method. The decomposition of a uranyl oxalate solution is the best established method of actinometry.[1]

The photo-reaction of thionine with ferrous salts.[2] The dye thionine ("Lauth's violet") can be reduced reversibly by mild reducing agents to a colourless "leuco" form. The leuco form reacts readily with ferric salts and gives thionine again. The redox potential (p. 263) of the reaction thionine$+e^- \rightarrow$ leuco-thionine is such that the redox equilibrium with the ferrous–ferric system lies to the left-hand side in the equation thionine$+$Fe^{++} $\rightleftharpoons$ leuco-thionine$+$Fe^{+++}. However, by supplying energy in the form of light (absorbed by the thionine) one can cause the reaction to proceed to the right. As the concentration of products increases, the spontaneous reversal of the reaction ("dark reaction") becomes more rapid, and, clearly, with a given intensity of light a *photo-stationary equilibrium* is eventually reached. (Incidentally, the redox potential of the solution will be altered by the photochemical reaction; this provides one type of photo-voltaic effect.) The rate of the dark reaction increases with rise of temperature whereas the photochemical bleaching reaction is substantially independent of temperature.

Thionine solutions show a faint red fluorescence; this can best be seen by examining the solution at right angles to a powerful narrow beam of white light in a dark room. The primary process is therefore excitation of the thionine. The excited molecule can either return to its ground state with the emission of fluorescence, or it may react with a ferrous ion, capturing an electron from it. Consequently, addition of ferrous salt "quenches" the fluorescence.

EXPERIMENT

Investigate the photochemical reaction between thionine and ferrous sulphate.
Procedure.

(a) *Determination of the absorption spectrum.* See p. 161 for methods of spectrophotometry. Thionine is a dye which does not obey Beer's Law accurately; with increasing concentration of dye, a dimer (or aggregate?) is formed which has a slightly different absorption spectrum.[2] The absorption spectrum should therefore be determined over a range of concentrations, using cells of different optical length (e.g. 0·1, 1, and 10 cm with solutions containing 1, 0·1, and 0·01 g/litre). A stock solution (e.g. 100 ml) of thionine containing 1 g/litre should first be made up and carefully *filtered*. This stock is used for preparing other solutions as required.

Instead of a complete determination of the absorption spectrum, the region of absorption can be ascertained approximately by means of a simple "colorimeter" (absorptiometer) (p. 167) in conjunction with different filters.

The absorption spectrum of thionine has been reported by
Rabinowitsch and Epstein.[2]

(b) *Absorption and fluorescence.* Set up a sodium lamp (p. 150)
or an intense tungsten filament lamp with a filter transmitting in
the yellow-green region, and, by means of a lens and diaphragms,
produce a strong, narrow beam of yellow light. Direct the beam
horizontally through a cell about 10 cm long containing successively
thionine solutions of 1, 0·1, and 0·01 g/litre, and examine the solution
at right angles to the light beam. A red fluorescence can be seen,
and from the distribution of the fluorescence it can be seen where
the light is being absorbed. A darkened room is desirable for these
observations. Confirm by use of other filters or by using a wave-
length spectrometer as monochromator (p. 153) that light of spectral
regions not strongly absorbed by the dye does not cause fluorescence.
Note that the fluorescent light is of longer wavelength than the
absorbed light, i.e. of smaller energy.
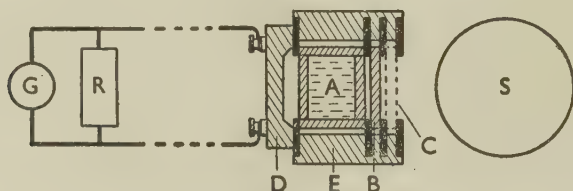
Fig. 13.4. Apparatus for determining the rate of bleaching of a
solution of thionine.

Investigate qualitatively the effect of additions of ferrous sulphate
to the dye solution on the intensity of fluorescence.

(c) *Kinetics of the bleaching reaction.* The apparatus shown in
Fig. 13.4 is required (cf. p. 169.) The essential parts are: S,
a sodium lamp or 150-watt pearl tungsten lamp with a yellow-green
filter: A, an optical cell, e.g. 1 cm thick, 1·25 cm wide and 5 cm high:
B, a piece of heat-absorbing glass: C, a sliding metal plate to act as
shutter: D, a rectangular barrier-layer photocell (p. 166): G, a
galvanometer with variable shunt, R. G is preferably of the type
shown in Fig. 12.5. Suitable characteristics are an internal resistance
of about 100 Ω and a maximum sensitivity of about 200 mm/μA.
It must be possible to reduce the sensitivity by factors of 10 and 100
by means of the shunt. E is a wooden mount for the cells. The
whole of the solution in the cell A must be illuminated, and the
stops must allow only light which has passed through the solution
to fall on the photocell.

Solutions. A suitable reaction mixture contains about 1 mg of
thionine, 0·1 g phosphoric acid, and 0·1 g of ferrous sulphate. The

phosphoric acid is added to repress hydrolysis of the iron salt and to reduce the effective ferric ion concentration by complex formation, thus slowing the "dark", reversal reaction.   Note that *the above reaction mixture cannot be kept for more than a quarter of an hour* as the ferrous salt is rather quickly oxidized by dissolved air, and the photo-reaction is then greatly inhibited.   It is best, therefore, to make 500 ml of a stock solution containing 50 mg of thionine and 3 ml of syrupy phosphoric acid; then take 10 ml portions of this stock, add 50 ml of de-aerated water and 0·1 g of powdered ferrous sulphate crystals.   Dissolve the crystals quickly and perform the measurements at once.

Measurements.   Clean the cell and fill it with distilled water. Arrange the sodium lamp close to the cell-holder so as to obtain a full-scale deflection of the galvanometer with the shunt set for lowest sensitivity (i.e. about 1/100th of full sensitivity).   Allow the lamp to run for $\frac{1}{2}$ hour to become steady, and then read the galvanometer zero (shutter closed) and full deflection (shutter open) several times. Close the shutter, empty the cell, and refill it with the standard reaction mixture, freshly made up from the stock solution as described above.   Open the shutter, start a clock, and read the galvanometer deflection every 15 seconds at first, and then less frequently as the reaction slows down.   At first, the deflection should be only a few per cent of full scale, but it should gradually increase as the dye bleaches, and eventually come to a constant value.   This indicates the photo-stationary equilibrium where the rate of bleaching by light is equal to the rate of thermal back-reaction.   Then close the shutter, check the zero, and read again the deflection with pure water to see whether the lamp intensity has altered during the experiment.

Repeat the experiment with a fresh sample of mixture to ascertain whether the kinetics are reproducible.   Then repeat the readings with two or three lower light intensities.   For this purpose, the lamp should be moved away from the cell a little so that the deflection with water is 75, 50, and 25% of that employed in the first experiment.   (When the intensity has been adjusted and measured in this way, one can alter the shunt, if desired, to produce a conveniently large deflection for taking the kinetic readings.)

Carry out two or three more kinetic determinations at a fixed light intensity but with different amounts of added ferrous sulphate.

(d) *Kinetics of the thermal* ("*dark*") *back-reaction.*   The reversal of the photo-reaction can be followed by using a very low light intensity.   Move the lamp away from the cell until full-scale deflection of the galvanometer at maximum sensitivity is obtained with water in the cell.   Then empty the cell and fill it with fresh reaction

mixture.   Bleach the mixture as fully as possible by exposing it near a tungsten filament lamp, interposing a cell of water to protect the solution from the heat of the lamp.   When the solution has bleached, transfer the cell *as quickly as possible* to the photometric apparatus and take galvanometer readings at once and then every $\frac{1}{4}$ minute, etc.   Continue the readings until a steady value is reached. If the reaction is completely reversible, the colour should return fully, and the light transmission should then equal that of a fresh, unbleached solution.

Repeat the measurements with (i) a solution which has been cooled somewhat below room temperature (but not to the dew-point), and (ii) another which has been warmed to about $30°$ C.

Also make two or three dark-reaction measurements with solutions to which small, known amounts of ferric salt have been added.

Results.   In each series of galvanometer–time readings the lamp intensity may have changed a little from beginning to end of the readings.   A correction can be applied by assuming that the drift was linear with time. Thus one can calculate the fraction of light transmitted by the solution, I_t/I_0, for each reading.   For the present purpose the small deviations from Beer's law are negligible, and hence the optical density, $D = \log (I_0/I_t)$, is a linear measure of the concentration (p. 160).   Plot all the results in the form of graphs of D against t to show how the concentration of dye decreases with illumination or increases in the dark (or, rather, under very feeble illumination).

The form of the bleaching curves is mathematically complicated, especially as the solution has not been kept stirred, but the general form of the kinetics can be elucidated by the following approximate analysis. In the early stages of the bleaching (e.g. for the first 20% of change) the back-reaction is negligible and the slope of the concentration–time line, which is approximately linear, can be taken as a measure of the rate of the photochemical reaction.   It should be noted that the first few points on the graph are liable to be less accurate than later ones as they represent small deflections; hence, the best mean slope over the first 20% of the graph should be taken.   Plot graphs to show the influence of (i) light intensity, and (ii) ferrous ion concentration on the rate of bleaching.

Note also the effect of these two factors on the concentration of thionine present in the photo-stationary mixtures. Explain the observations qualitatively.

Examine the kinetics of the dark reaction for conformity to 1st- or 2nd-order kinetics in the usual way.   Since the reactions involved are thionine $+ Fe^{++} \rightleftarrows$ leuco-base $+ Fe^{+++}$ one might expect the reverse reaction (in the absence of added ferric salt) to be of 2nd order.   At any stage the concentration of leuco-base and also that of Fe^{+++} should be equal to (original dye concentration *minus* observed dye concentration) and this is the quantity to be used when examining the kinetics of the back-reaction.   On the other hand, if an excess of Fe^{+++} is present, either as a deliberate addition or as a result of oxidation of ferrous salt

by dissolved air, then the kinetics of the dark reaction would be expected to follow the 1st-order law.

Experiments at different temperatures should show that the photo-chemical (forward) reaction is practically independent of temperature, whereas the dark reaction accelerates with temperature in the normal way.

The detailed *mechanism* of this photochemical reaction is probably much more complicated than might be supposed from the elementary discussion given above. This is frequently the case in such studies; the overall kinetics may not lead directly to all the details of the mechanism.

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CHAPTER 14

SURFACE CHEMISTRY AND COLLOIDS

Introduction.

Surface chemistry is a special branch of Physical Chemistry; at a boundary between two phases there is necessarily a rather abrupt change in the nature or intensity of the inter-molecular forces, and this fact gives rise to a number of phenomena which have no counterpart in homogeneous systems. The chief of these are *adsorption, molecular orientation* in monolayers, and the formation of *electrical double layers*; other phenomena of surface chemistry may be considered as secondary effects.

Surface phenomena are rarely important, however, unless the system has a relatively large amount of interfacial area per unit mass. Consequently, surface effects are generally noticed most clearly in connection with very thin films, highly porous solids or finely-divided dispersions of one phase in another. The latter category includes particularly *colloids*.

Colloid chemistry is best defined as the study of submicroscopic dispersions, but the term "colloid" is often used to include coarse suspensions, emulsions, films, plastics, etc.—in fact, any material which is not obviously "crystalloidal". In this sense, colloids include the great majority of materials used in industrial chemistry, and consequently colloid chemistry has great technological importance. However, much of the content of classical colloid chemistry is descriptive and qualitative, and it is only with the development of surface chemistry and of high polymer chemistry that it has become possible to find theoretical interpretations of some of the numerous phenomena that are known.

14A. SURFACE CHEMISTRY

Adsorption by solids. Adsorption is the accumulation of a substance at an interface. It is met with at all types of interface, notably, gas–solid, solution–solid, solution–gas, solution α–solution β interfaces. Two principal types of adsorption are recognized; *physical adsorption* is non-specific, rapid and reversible, the *adsorbate* being held at the interface only by dispersion and polarization forces, whereas *chemisorption* (such as occurs when gases are brought

into contact with truly clean metallic surfaces), is simply the forma-
tion of a two-dimensional compound.   A subsidiary type of chemi-
sorption is *ionic exchange adsorption*, as exemplified by the adsorp-
tion of cationic dyes by acidic oxides (e.g. silica) and of anionic dyes
by basic oxides (e.g. ZnO); here an insoluble surface salt is formed.
However, the unqualified term "adsorption" will generally refer to
a reversible, physical adsorption.

The amount of substance adsorbed at any surface decreases with
rise of temperature, since all adsorption processes are exothermic.
At constant temperature the amount adsorbed increases with the
concentration of the adsorbate (in the gas phase or in solution), and
the relationship between amount adsorbed (x) and the concentration
(c) is known as the *adsorption isotherm*.   Only at very low concentra-
tions is x proportional to c.   Generally the amount adsorbed in-
creases less than proportionally to the concentration owing to the
gradual saturation of the surface, and in many cases the isotherm
can be fitted to an equation of the form $x = kc^n$, where $n<1$.   This
expression, generally known as the Freundlich adsorption isotherm,
is empirical and lacks theoretical basis.

A more significant isotherm is that of Langmuir which was
derived originally by a simple theory for the case of physical adsorp-
tion of a gas on a plane solid surface, assuming that a layer only
one molecule thick could be adsorbed.   This isotherm is of the form

$$x = \frac{abc}{1+ac}$$

where a and b are constants for a given system.

Neither the Freundlich nor the Langmuir equation is capable of
representing the S-shaped ("sigmoid") isotherms which are obtained
when the adsorption of vapours on a porous solid is studied at rela-
tively high vapour pressures (approaching saturation).   A more
complicated equation must then be used, the best-known being the
isotherm of Brunaer, Emmett, and Teller (1938).[1]   This equation
was arrived at on the assumption (confirmed by Harkins and Jura [2])
that *multimolecular adsorption* can take place.   The equation is

$$\frac{p/p_0}{x(1-p/p_0)} = \frac{1}{x_m c} + \frac{(c-1)}{x_m c} \cdot \frac{p}{p_0}$$

where x is the amount of vapour adsorbed at a partial pressure p,
p_0 is the saturation pressure, x_m is the amount of vapour which would
be required to form a monomolecular layer over the surface, and
c is a constant.   This equation (the "B.E.T. isotherm") represents
fairly satisfactorily the adsorption of water by textiles, silica gel,
etc., and of many vapours by finely divided powders.   It is much
used for determining the surface areas of powders.

EXPERIMENT

Determine the adsorption isotherm of oxalic acid from aqueous solution by charcoal.

Procedure. Prepare 1 litre of $0.5N$ oxalic acid solution and titrate 10 ml portions of it with approx. $0.1N$ $KMnO_4$ solution in the usual way (adding sulphuric acid and warming to $80°$ C). Hence calculate the true concentration of the $KMnO_4$.

Clean and dry 7 stoppered reagent bottles and weigh accurately into each about 2 g of finely ground charcoal. (The kind sold for decolorizing solutions is particularly suitable.) To the first bottle add 50 ml of $0.5N$ oxalic acid and 50 ml of water. Place the bottle in a shaking-machine and shake for successive $\frac{1}{4}$-hour periods. Take out a 10 ml sample after each shaking and titrate it with the permanganate solution. These tests will show how rapidly the adsorption proceeds. Note the time required for a constant concentration to be reached. In the main set of experiments shake the bottles for at least 50% longer than the minimum time indicated by these preliminary tests.

Meanwhile, into the other 6 bottles pipette 100, 80, 60, 40, 20, and 10 ml of the $0.5N$ oxalic acid, and add 0, 20, 40, 60, 80 and 90 ml of distilled water respectively, thus starting the experiments with 2 g samples immersed in 100 ml of 0·5, 0·4, 0·3, 0·2, 0·1, and $0.05N$ oxalic acid. Shake the bottles for the time mentioned above, and then filter the contents through *small* filter-papers, rejecting the first 10–20 ml portions of filtrate from each bottle in case there should be any adsorption of oxalic acid or of water by the filter paper. (If time permits, this point should be investigated experimentally.) It should be possible to collect at least 80 ml of each filtrate, and this quantity will provide two 25 ml portions for duplicate titrations, and, if these do not agree, a third portion for a check.

Calculation. Calculate (a) the *final* concentration of the solution C_s, (b) the weight of oxalic acid removed by adsorption, x, (c) the amount of adsorption per g of charcoal, x/m. Plot x/m against C_s. To test the applicability of the Freundlich isotherm plot $\log (x/m)$ against $\log C_s$. If a straight line is obtained, calculate the constants in the equation $x/m = kc^n$.

The applicability of the Langmuir isotherm can be tested similarly by plotting m/x against $1/C_s$.

Other experiments. 1. The adsorption of an anionic detergent can be used to determine relative surface areas of ZnO pigments.[3]

2. Reactions of salt solutions with ion-exchange resins in some ways simulate adsorption processes.[4]

3. The adsorption of simple anionic ("acid") dyes such as Orange II by the amphoteric fibre, wool, can be shown to increase with addition of HCl, demonstrating that the adsorption is an exchange reaction of the

form $Wool^+Cl^- + Na^+Dye^- \rightarrow Wool-Dye + NaCl$. On the other hand, adsorption of "direct cotton dyes" by cellulose is a case of direct adsorption of the whole dye salt and is therefore increased by addition of sodium chloride by virtue of the common ion effect.

4. Qualitative experiments may be made on the separation of dyes, natural pigments, etc., by *chromatography* on a column of alumina. Chromatography depends on slight differences in adsorption affinity.[5]

Adsorption at liquid surfaces. Adsorption occurs at the gas–liquid interface and the liquid–liquid interface, although it cannot be measured as readily as adsorption by solids. Further, the adsorption is not strong unless the substance possesses a certain type of molecular structure. Substances which are strongly adsorbed at the air–water or oil–water interfaces are called *surface-active*, and are found to have an "amphipathic" structure—that is, within the same molecule there are water-soluble (*hydrophilic*) and water-insoluble (*hydrophobic*) molecular groups. The *paraffin chain salts* (e.g. natural and synthetic soaps) are the best examples of highly surface-active substances. Simple inorganic salts are *negatively adsorbed*; in other words, water is more surface-active than salt.

EXPERIMENT

Verify the adsorption of a surface-active dye at the air–water interface.

Procedure. Set up a large "chromatography tube", *A*, Fig. 14.1, having a coarse sintered disc, *B*, at the bottom. Fit it with a wide delivery tube, *C*, at the top. Prepare a dilute aqueous solution of "Carbolan Crimson" (Imperial Chemical Industries

Fig. 14.1. Demonstration of the adsorption of "Carbolan Crimson" dye at the air-solution interface.

Ltd.), and pour enough into the column to half fill it. Pass a stream of air upwards through the column, and regulate the amount so that a column of froth rises slowly and passes over into the receiving flask *D*.

When sufficient liquid has been collected in *D*, pour a sample into a test-tube and place it beside similar test-tubes containing (i) the original dye solution, and (ii) the residue left in tube *A*.

Provided the solution used is not too concentrated, it will be observed that the liquid produced from the froth contains *more* dye than the original solution, and the residue contains less.

Adsorption and surface tension. It is a thermodynamic consequence of positive adsorption of a solute that the surface (or

interfacial) tension is lowered; conversely, negatively adsorbed solutes (e.g. salts) cause a rise of surface tension. The Gibbs adsorption equation gives the quantitative relationship between concentration, adsorption, and change of surface tension. For the special case of a very dilute solution of a non-ionic surface-active substance, this equation takes the simple form

$$\Gamma = -\frac{C}{RT} \cdot \frac{\mathrm{d}\gamma}{\mathrm{d}C}$$

where Γ is the mass of solute adsorbed *per unit area of the surface* from a solution of concentration C and surface tension γ. (In the exact form of the equation the *activity* of the solute takes the place of concentration). This equation has been checked experimentally in several ways, the measurement of Γ being the chief obstacle. Conversely, a study of γ–C curves can be used to deduce the extent of adsorption.

EXPERIMENT

(*a*) *Investigate the influence of chain-length on the surface activity of normal aliphatic alcohols.* (*b*) *Determine the surface tension–concentration curve for n-amyl alcohol, and hence calculate the adsorption.*

Procedure. (a) For this part of the experiment any of the ordinary methods of measuring surface tension (Ch. 5) may be used, since high accuracy is not needed; the apparatus described below for part (b) is equally suitable for (a).

Prepare $0.1M$ solutions of methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl alcohols by delivering 0.40, 0.58, 0.75, 0.92, and 1.08 ml of the alcohols respectively with a graduated 1-ml pipette into clean 100-ml standard flasks, and make the solutions up to the mark with distilled water. (If the amyl alcohol is found to leave a small residue of oily drops the solution should be discarded and the amyl alcohol purified by careful distillation with an efficient fractionating column.) Determine the surface tensions of the solutions at 20° C, and represent the results by a graph showing surface tension as a function of number of carbon atoms. The lowering of surface tension by a dilute solution of a substance can be taken as a measure of its "surface activity".

(b) For this part of the experiment it is necessary to measure small differences of surface tension, and, further, extreme care is needed to avoid the minute amounts of contamination which would vitiate the results. The all-glass differential U-tube apparatus shown in Fig. 14.2 is suitable, as small differences of liquid level can be measured by means of a travelling microscope, and the whole apparatus

can be immersed in a cleaning mixture before use.   The two capillary tubes, *a* and *b*, are about 0·25 and 0·05 cm in radius, and should be selected for uniformity of bore before the apparatus is made, the length of a pellet of mercury being compared in different parts.

After thorough cleaning in chromic-sulphuric acid mixture, the apparatus is washed with a jet of distilled water.   From then on, care must be taken not to touch the ends *c* and *d* with the fingers, as invisible films of grease may travel on glass surfaces.

The tube is filled with distilled water through the funnel *d*, and the excess poured out through the side tube *c* by tilting the tube. Small quantities can be taken off with the aid of a clean strip of filter paper.   The tube is then set up accurately vertical, preferably in a glass-sided tank of water at 20° C, and the difference between the heights of liquid in the two tubes is measured accurately with a travelling microscope.   The tube is then rinsed out again with water, and another reading is taken.   If the readings cannot be repeated to within 0·1 mm the apparatus is not clean.

Now proceed to determine the difference of level using 0·01, 0·02, 0·05 and 0·1*M* solutions of amyl alcohol, in that order.

Results.   Plot a graph of the results, showing γ against *C*.   Draw a smooth curve through the points and then construct tangents at $C = 0.01, 0.02, 0.04,$ 0·06, and 0·08.   Measure $d\gamma/dC$ from the slopes of these tangents, and hence calculate values for Γ, applying the approximate form of the Gibbs equation (see above).   Since γ is in dynes per cm, *R* must be in ergs $(R = 8.313 \times 10^7$ ergs per mole per degree).

Fig. 14.2. Differential U-tube for determining the influence of solutes on surface tension.

Note that Γ tends to a constant value at higher concentrations; estimate this limiting value and calculate $1/\Gamma$, which gives the area in the surface per mole of adsorbed amyl alcohol.   Calculate the value of $10^{16}/N\Gamma$ (where *N* is Avogadro's number, $= 6.03 \times 10^{23}$). This expression gives the area in Å² occupied per molecule.   Compare the result with the molecular dimensions of amyl alcohol, and deduce the thickness of the layer.   (The cross-sectional area of a paraffin chain in a crystalline paraffin is about 19·5 Å².)

The spreading of oils.   When a small drop of an insoluble oil is placed on a *clean* water surface it may behave in one of three ways: (a) remain as a *lens*, if it is a "non-spreading" oil, (b) spread as a thin film which may show interference colours, until it is uniformly distributed over the whole surface of the water, forming a so-called "duplex" film of appreciable thickness, (c) spread as an invisible monolayer, leaving excess oil as a lens in equilibrium.

The spreading behaviour is determined by the *cohesion* of the liquid (i.e. mutual attraction between its molecules) and its *adhesion* to water. Cohesion is measured by the surface tension of the liquid against air and adhesion to water by the interfacial tension, oil–water. By considering the forces acting at the circumference of a floating oil drop, the criterion for spreading can be seen to be that the *total* surface free energy must decrease. The free energy decrease is called the *spreading coefficient W*, and is given by

$$W = -\gamma_A + \gamma_B - \gamma_{AB}$$

where γ_A, γ_B, and γ_{AB} are the surface tensions of the two liquids A and B and their interfacial tension. If W is positive, liquid A will spread on liquid B. One must bear in mind that γ_A and γ_B will be to some extent different for the pure liquids and for the mutually saturated liquids. According to Harkins, even where the initial spreading coefficient is positive for the pure liquids, the *final* spreading coefficient is negative, i.e. initial spreading is followed by retraction into small lenses.

EXPERIMENT

Investigate the spreading behaviour of benzene, "Nujol" (medicinal paraffin), and "Nujol"+0·1% oleic acid on a clean water surface and on water contaminated by oleic acid.

Procedure. Thoroughly clean a large photographic dish with warm soap solution and wash it thoroughly in a sink under running water. Set the dish level in the sink and run in water until it overflows. This procedure secures, at least temporarily, a water surface which is substantially clean. To test for the presence or absence of contamination on a water surface one can sprinkle on a trace of pure talc powder and then slowly "sweep" the surface with a long strip of "Perspex" which has been cleaned with soap and freshly rinsed under a running tap. The "Perspex" must not be touched with the fingers except at the very ends (which project well beyond the dish). If the water surface is contaminated one observes the talc to move before the barrier actually reaches it. The ease with which a surface is contaminated can be readily demonstrated by touching a clean water surface bearing talc with a human hair or a tiny crystal of cetyl alcohol.

Having prepared a clean water surface, make the observations of spreading behaviour by placing one very small drop of the oil on the water. The dish must be washed thoroughly between each experiment. In the case of "Nujol"+oleic acid, a duplex film showing interference colours can be obtained, and the colours can be changed by "compressing" the film by means of the "Perspex" strip.

Interpret the observations by reference to the following surface and interfacial tension data.

| Liquid | Surface tension | | Interfacial tension against water | Surface tension of water satd. with liquid |
	dry	satd. with H_2O		
Benzene	29	29	35	62
"Nujol"	34	—	53	73
Oleic acid	33	—	16	—

Insoluble monolayers on water. The invisible films demonstrated in the last experiment to spread spontaneously with oleic acid or cetyl alcohol are known to be one molecule thick. Stable monolayers are obtained with substances possessing both hydrophobic and hydrophilic portions in the same molecule. The latter may be $-COOH$, $-OH$, $-NH_2$, $-CN$, etc. Such ("head") groups are "attracted" to the water because of their electric dipole, and they serve to "anchor" the molecules on the water surface, while the hydrophobic portion of the molecule—generally a hydrocarbon chain—is highly insoluble in water. Not all such substances, however, spread spontaneously over water to any appreciable extent, but many can be obtained as a monolayer by applying them to the surface of the water in the form of a solution in a spreading, volatile solvent, e.g. benzene.

Monolayers on water exhibit the following properties. (a) They can be "handled" as though they were an elastic skin on the water. They can be retained intact on the water if the sides of the vessel are made hydrophobic, and the monolayer can then be compressed or expanded by hydrophobic barriers moved on the surface. Waxed paper strips, chromium-plated rods or strips of "Perspex" can be used as barriers. (b) Monolayers exert a two-dimensional pressure which can move light floating particles such as talc powder or a fine vaselined thread. (c) Monolayers lower the surface tension of the water on which they float. The reduction of surface tension is called the "*surface pressure*" (F) of the monolayer, since it is equal to the two-dimensional pressure mentioned in (b). The surface pressure varies with the area (A), and F–A curves for different substances show a variety of different forms corresponding roughly to solid, liquid and gaseous states.

The surface pressure has most often been measured by the horizontal *film balance* (Langmuir 1917, Adam 1926), in which the actual thrust on a barrier is determined by means of a torsion balance. In recent years the *vertical* film balance, developed by Dervichian

(1935) and Harkins and Anderson (1937) [6] has come into general
use. This is based on Wilhelmy's surface-tension method, and is
shown diagrammatically in Fig. 14.3. *A* is a thin glass cover-slip,
suspended from the balance *B*, the beam of which carries a small
galvanometer mirror *C*. *A* dips into a shallow trough of water *F*,
the edges of which are hydrophobic. The balance is brought to its
normal zero by means of weights, and then the monolayer is applied
to the water surface. There is a reduction of downward pull on the
cover-slip of $F \times p$, where p is the perimeter of the plate. The
balance therefore rises on the left by an amount determined chiefly
by the thickness of the plate (reduced buoyancy). The deflection
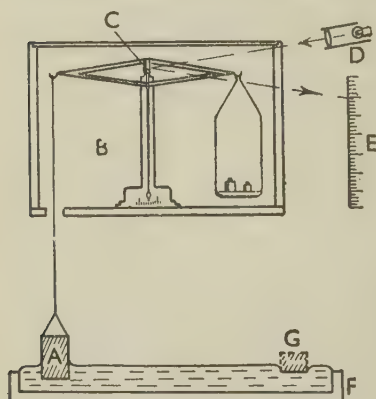
Fig. 14.3. Principle of the vertical surface film balance.

of the beam, previously cali-
brated in terms of grams, is read
accurately by a lamp *D* and
scale *E*. One then proceeds
to move the barrier *G* to a new
position and read the corres-
ponding deflection of the spot of
light on the scale *E*, thus obtain-
ing values of *F* at different film
areas. An apparatus for auto-
matically recording *F–A* graphs
has been developed on this prin-
ciple.

If a surface film is "com-
pressed" too much—that is,
beyond the area needed for close-
packing of the molecules—it
crumples irreversibly, and a visible pellicle is formed.

A simple apparatus for detecting surface films. For many pur-
poses a very simple method can be used for measuring surface
pressures approximately, use being made of the capillary rise of a
liquid between two parallel glass plates separated by a small gap.
The meniscus between the plates is, of course, in connection with
the surface of the trough *via* the narrow strips of water at the edges
of the plates, and consequently any change in the surface tension
of the water is registered by a corresponding change in the level of
the meniscus.*

* It is interesting to record that this idea was used as long ago as 1890 by
Lord Rayleigh, who employed it to demonstrate to an audience at the Royal
Institution the reduction in the surface tension of water by traces of oil, an image
of the meniscus being projected on a screen. The parallel plate apparatus may
therefore be said to be the earliest "film balance". Rayleigh later abandoned
it because he suspected, on the authority of Quincke, that the angle of contact
might not be zero—a matter which is no longer in doubt, at least for a receding
meniscus.

A convenient form of the "film indicator" is shown in Fig. 14.4. It is made from two strips of best quality plate glass $10 \times 1 \times 0.6$ cm. Plate glass is usually nearly optically plane; it is easily tested by observing the interference bands produced when two clean pieces are "wrung" together. Thinner glass is usually inferior in flatness.

The plates are separated by a gap of about 0.6 mm obtained by inserting over the upper half a spacer made of three microscope cover-glasses $5 \times 1.2 \times 0.02$ cm. Each of these is selected for uniformity of thickness by measurement with a micrometer, and it is not difficult to find three which together form a spacer which does not vary by more than 0.005 mm from end to end. The plates are clamped together by two ordinary screw clips (C) with rubber washers. This arrangement ensures that the gap between the lower half of the plates is uniform. The dimensions of the apparatus are not critical.

Since it is difficult to cut plate glass exactly to size, the inner edges of the strips may be bevelled off at $45°$ by grinding with carborundum powder until the two pieces are parallel and of the same width. Once made, the device need not be dismantled; it is scrupulously cleaned before use by immersing the lower half in cleaning mixture.

Fig. 14.4. Simple apparatus for detecting surface films.

Clean water rises about 2.5 cm in an apparatus of the size recommended; the meniscus is of the form shown in Fig. 14.4 (D), and makes an excellent mark on which to focus the cross-wires of a travelling microscope. On the other hand, it is very difficult to focus a microscope on the wide water level in the trough, but this difficulty is avoided by arranging a thin glass fibre to dip into the water at an angle between the glass device and the microscope, when the fibre and its reflection form an arrow pointing to the precise water surface. If the capillary rise between the plates is read to the nearest 0.005 cm the sensitivity of the apparatus is about 0.1 dyne per cm. If the device is required merely to indicate the effect of a film on the surface tension it is only necessary to observe the position of the meniscus, as the absolute capillary rise may not be needed.

When the film is applied and compressed in the usual way the meniscus falls progressively, and its level is measured at a series of diminishing film areas. Like the vertical balance, the capillary apparatus is not suitable for measurements with increasing film

areas, as a monolayer may be deposited on the glass by the meniscus as it falls, making the glass hydrophobic.

In using the device for the approximate or comparative measurements for which it is intended, it is sufficient to assume that the rise is proportional to the surface tension, as for infinite plates,

$$h = \frac{2\gamma}{bg\rho}$$

where b is the distance between the plates and ρ the density. Thus the initial reading with clean water is taken as a calibration of the apparatus by assuming the surface tension of water at the temperature of the experiment. This is not accurately true, partly because the plates are narrow and partly because the spacing is too wide for the meniscus to be semi-circular in cross-section.

EXPERIMENT

Determine the surface area occupied by a close-packed, condensed monolayer of cholesterol.

Procedure. Thoroughly clean a shallow rectangular "Perspex" trough with hot soap solution, followed by washing under the tap. Thereafter keep the trough covered with a glass plate when not in use and avoid touching any part of its working area. Level the trough and fill it with tap water until the water stands slightly above the level of the flat sides. Connect the overflow pipe to the sink. Meanwhile, prepare about 100 ml of freshly distilled benzene, collecting direct into a clean stoppered 100 ml flask, and taking some to rinse all parts of the apparatus beforehand to remove possible contamination present on the glass.

Weigh out as accurately as possible about 0·025 g of cholesterol into a scrupulously cleaned 25 ml stoppered standard flask, and make up to the mark with the freshly prepared benzene.

Before applying the film, the surface of the water in the trough must be cleaned by repeatedly "wiping" it with freshly rinsed chromium-plated or "Perspex" rods. Any contaminating film may be collected and confined behind a barrier at one end of the trough. To test the cleanliness of the surface, sprinkle on a little talc powder and observe it carefully while a barrier is moved along the trough; the presence of a film is indicated by movement of the talc particles before the barrier actually reaches them. Scrupulous care is needed to get a properly clean surface. (A simple test with talc will show how a film spreads immediately from any ordinary object which is allowed to touch the water.)

As soon as the surface is proved clean, set up the glass plate film indicator (freshly cleaned and rinsed under the tap) at one end of

the trough, and focus a travelling microscope on the meniscus without delay. Then drop on to the water about 0·1 ml of the cholesterol solution, preferably measured by a calibrated micrometer syringe (p. 100), but otherwise by a micropipette or small weight pipette.

Advance a barrier slowly in stages along the trough, thus slowly compressing the film. Measure the area occupied by the film and the position of the meniscus in the indicator at each stage. When the film becomes nearly close-packed the surface tension, and hence the meniscus, will fall rather rapidly with decrease of area. Obtain enough points to plot a curve of "capillarity" against area. Hence calculate the area occupied by a molecule of cholesterol. Repeat the whole experiment with slightly different quantities of cholesterol.

Calculate the approximate thickness of the film, assuming that the cholesterol monolayer has the same density as cholesterol crystals.

The electrical double layer. Electrical double layers are formed at interfaces by preferential adsorption of one of the ions of an electrolyte. Two extreme cases can be distinguished; chemically *inert* surfaces (e.g. paraffin, oil, quartz) receive a "charge" only by adsorption of a foreign ion, whereas intrinsically *ionogenic surfaces* (e.g. sparingly soluble salts, proteins, clays, etc.) release ions by simple interaction with water.

Almost invariably, substances in contact with dilute aqueous solutions are found to carry a "charge" as shown by the fact that small particles of the material will migrate through water in the presence of an electric field—the phenomenon of *electrophoresis*. However, the "charge" is not a net electrostatic charge detectable by an electroscope, but a double layer of ions. An excess of ions of one charge is firmly attached to the surface, while an equivalent quantity of ions of the opposite charge exists free in the solution. The free ions are held in the vicinity of the surface by electrostatic attraction. Electrophoresis and the three other *electro-kinetic* effects (namely, *electro-osmosis, streaming potentials* and *sedimentation potentials*) arise when attempts are made to shear off the mobile part of the double layer from the surface. The four electro-kinetic effects are physically equivalent, and any one of them may be used to study the nature of the electrical double layer. The basic theory of these effects was given by Helmholtz, but the quantitative interpretation of them is not entirely satisfactory, and results of electrokinetic measurements should be reported directly in terms of the measured quantities (e.g. the rate of migration of particles in electrophoresis (see p. 340).

EXPERIMENT

*Determine by means of electro-osmosis the sign of the charge on
cellulose in contact with water and with various dilute salt solutions.*

Procedure.   The simple apparatus shown in Fig. 14.5 may be used
for semi-quantitative measurements of electro-osmosis.   It consists
of a U-tube, constructed in three pieces, A, B, and C, which can be
fitted together by means of the ground glass joints, a,a.   Platinum
electrodes, c,c, are sealed into each limb, and the side B is of semi-
capillary tubing to magnify the rate of movement of the liquid.   A
scale, d, is placed against this tube.

Macerate some filter paper with a little distilled water, and pack
a plug of the paste fairly tightly into the middle of tube A.   Then
fit the tubes together and fill the whole apparatus with distilled
water, taking care to exclude air bubbles.   Arrange the height of
water so that the meniscus in B
stands half-way up the scale, and
allow the apparatus to stand
until the levels are steady.   Read
the meniscus on the scale.

Now switch on 220 V d.c. from
the mains or dry batteries,
noting the polarity.   Read the
position of the meniscus at suit-
able intervals of time and then
reverse the connections and
measure the reversed movement.
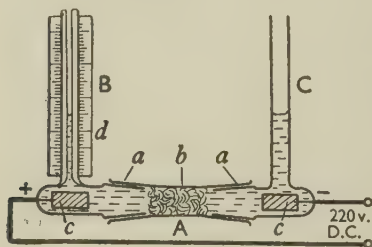
Fig. 14.5. Apparatus for study of
electro-osmosis.

Verify that the rate of electro-osmosis is approximately propor-
tional to the applied potential.

Disconnect the leads and dismantle the apparatus, but without
disturbing the filter-paper plug.   Re-connect A and C and fill C
with a $10^{-5}M$ solution of thorium nitrate, allowing the solution to
percolate through the plug.   Then repeat the measurements of
electro-osmosis.   Similar measurements may be made with very
dilute (10^{-3} to $10^{-5}M$) solutions of KCl, KOH, $K_4Fe(CN)_6$, a basic
dye such as methylene blue and a direct cotton dye such as Chlorazol
Sky Blue.   A fresh plug of filter paper must be used each time, and
therefore the flow with water should be measured first so that the
rates can be compared.

Results.   Express the results as the rate of electro-osmotic flow per volt
of applied potential, giving direction.   Cellulose itself is feebly nega-
tively charged—it carries some carboxyl groups.   This charge can be in-
creased by adsorption of OH^- ions or polyvalent anions, or decreased and
even reversed by polyvalent cations.   "Indifferent" electrolytes such as
KCl reduce the electro-kinetic effects without appreciably changing the
charge density.

Similar experiments may be made with other materials; for example, the iso-electric point of wool can be determined in such an apparatus, using dilute buffer solutions of different pH. At low pH values wool is cationic ($-NH_3^+Cl^-$) while at high pH values it is anionic ($-COO^-Na^+$). At the iso-electric point the number of $-NH_3^+$ and $-COO^-$ groups is equal.

The same type of apparatus can be used for measuring streaming potentials. Liquid from an external reservoir is flowed through the plug, and the p.d. set up between the two electrodes is measured on a valve potentiometer or pH-meter.

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14B. COLLOIDS

For the present purpose the term "colloids" will be restricted to *dispersions* of one phase in another. At one extreme one finds suspensions of solids in liquids, or of liquids in liquids—emulsions. Particles in the "sub-sieve range" (i.e. below about 50 microns) are sometimes called colloidal. With solid particles of sub-microscopic size ($<0 \cdot 1 \mu$) the dispersion is called a *sol*. The dividing line between a colloidal solution and a crystalloidal solution is equally vague and arbitrary; Graham's original criterion was the ability of the latter to diffuse through a parchment membrane, but one can readily prepare membranes (e.g. of collodion) with various pore sizes. True solutions of substances of high molecular weight (e.g. proteins) exhibit many of the characteristic properties of colloids. Others of low molecular weight owe their colloidal properties to the formation of *aggregates* of colloidal size (e.g. dyes, soaps).

A useful broad classification of colloids is into *lyophobic* and *lyophilic* types. Although many actual colloids are of intermediate

character, these concepts are clear-cut and assist in understanding the behaviour of colloids. A lyophobic colloid is essentially a dispersion of one phase in another of *unlike chemical type*. Such colloids therefore possess large interfacial free energy and are intrinsically unstable, or, at least, metastable. They owe their temporary stability to stabilizing agents, and, if these agents are removed, the colloids *coagulate*. The stabilizing agent may be an electrical double layer of adsorbed ions, or a film of adsorbed lyophilic colloid.

Lyophilic colloids are those which disperse readily in the solvent on account of solvation. They are, in fact, thermodynamically stable, molecular solutions, but exhibit colloidal properties on account of their high molecular weights (e.g. rubber in benzene, gelatine in water).

Lyophobic colloids. The chief characteristics of lyophobic colloids can best be illustrated by the following semi-quantitative experiments with emulsions (oil–water dispersions) and with two typical inorganic sols.

EXPERIMENT

Investigate the properties of emulsions by means of the following experiments, and interpret the observations.

(a) *Dispersion of liquid in liquid: emulsifying agents.* Attempt to disperse 5 ml of light paraffin oil (kerosene) in 100 ml of each of the following solutions, first by vigorous shaking and then by "homogenizing" the suspensions in a domestic cream machine: (i) distilled water, (ii) 1% sodium oleate solution, (iii) 1% gelatine solution, (iv) 1% suspension of bentonite (a finely divided clay) in distilled water. Also, pour a layer of olive oil as carefully as possible on to a solution which is approximately $0.001 M$ with respect to sodium oleate and $0.001 M$ with respect to sodium chloride.

Note the stability of the suspensions formed; distinguish between "creaming" and "breaking". Note the scattering of light by a very dilute emulsion.

(b) *Particle size.* Dilute 10 ml of each of the above emulsions (well mixed) with an equal volume of water in a test-tube. By means of a pipette remove 1 ml of the dilute emulsion from the middle of the tube and add to it 1 ml of warm 10% gelatine solution. Place a small drop of this final mixture on a microscope slide, put on a clean cover-glass, and allow the gel to set.

Examine the slides under a microscope with magnification of about $500 \times$. Describe the state of dispersion by noting the size of the largest and smallest oil drops observed and the chief range of size. The size can be found by reference to a scale placed in the

ocular of the microscope, and the magnification determined by use of a stage micrometer slide.

Careful examination of a very finely dispersed, dilute emulsion under high magnification will reveal the existence of *Brownian motion*—the continual random displacement of very small particles, caused by molecular bombardment.

(c) *Emulsion types.* Homogenize 50 ml of paraffin in 50 ml of 1% sodium oleate solution. Divide the emulsion into two equal parts and add to one a quantity of magnesium sulphate. Determine the emulsion type (that is, whether oil-in-water or water-in-oil) by the following tests: (i) add a few drops of the emulsion to water and to oil, and see with which it mixes readily. (ii) Add to one portion of emulsion an oil-soluble dye (e.g. "Oil Red"), and to another portion a water-soluble dye (e.g. methylene blue). The electrical conductivity can also be used to indicate whether oil or water is the *continuous phase*. Hydrophilic emulsifiers (sodium oleate, bentonite) favour oil-in-water emulsions; hydrophobic emulsifiers (magnesium oleate, carbon black) favour water-in-oil.

(d) *Viscosity of emulsions.* Prepare several emulsions of kerosene in 1% sodium oleate solution, using different proportions of kerosene, and measure their viscosities in an Ostwald viscometer (p. 89). The densities of the emulsions can be calculated from the volume composition of the emulsions, on the assumption that there is no volume change when oil is dispersed in water.

Why is an emulsion more viscous than either of its constituent liquids?

The viscosity of emulsions is not a very reproducible quantity since it depends on the degree of dispersion and *age* of the emulsion. Many colloids show *ageing*.

Furthermore, emulsions exhibit "anomalous" or "non-Newtonian" viscosity—that is, the apparent coefficient of viscosity depends on the *rate of shear* at which the measurement is made. With emulsions, the higher the rate of shear, the lower the apparent viscosity owing to the breakdown of the *structural viscosity*. (See Section 14C for the study of anomalous viscosity.)

(e) *Interfacial tension.* The effect of emulsifying agents (sodium oleate, gelatine) on the oil–water interfacial tension can be determined *approximately* by the drop-pipette. (Fig. 14.6 (a).) This has a bulb of capacity of about 1 ml and an up-turned jet which is ground smooth and sharp. With a given pair of liquids (oil–water) the *drop number* for a fixed volume is approximately inversely proportional to the interfacial tension. (For methods of measuring interfacial tensions accurately, see pp. 99–101.)

Most emulsifying agents lower the interfacial tension greatly and

thus facilitate dispersion. Extremely low interfacial tensions (<0.1 dyne/cm) lead to "spontaneous emulsification". A stable adsorbed film is, however, the chief factor in obtaining high *stability* in an emulsion.

(f) *Electrophoresis.* The stability of emulsions containing sodium oleate is closely associated with the presence of an electrical double layer which causes neighbouring droplets to repel each other, thus preventing coalescence. The presence of the double layer can be demonstrated most easily by electrophoresis, using an inverted U-tube as shown in Fig. 14.6 (b). The tube is first filled with the dispersion medium, dilute sodium oleate solution. The emulsion is then slowly introduced through the capillary stopcock from a small funnel. When sharp boundaries have been formed in both limbs, the tap is closed and the position of the boundaries is marked. The electrodes are then connected to the 220 V d.c. mains, and the direction and rate of migration of the boundaries is noted. Calculate the speed of migration approximately in cm/second/volt/cm.

It is evident that the oleate ions are strongly adsorbed at the oil–water interface, while the sodium ions provide the free "counter-ions" (*gegenions*) in the aqueous phase.

Inorganic sols. Classical colloid chemists devoted much attention to the methods of preparation and the properties of sols of metals, hydrated oxides, and sulphides. Only two examples, however, will be given here.

Fig. 14.6. Properties of emulsions.
(a) Interfacial tension.
(b) Electrophoresis.

EXPERIMENT

Prepare and study ferric hydroxide and arsenious sulphide sols.

(a) *Preparation of colloidal ferric hydroxide.* To a half-saturated, freshly prepared solution of ferric chloride add, in drops and with stirring, an approximately $2N$ solution of ammonium carbonate, until the precipitate formed just ceases to be dissolved. Filter if necessary and dialyze the liquid in a cellophane tube against distilled water until only a trace of chloride can be detected in the water.

Or, add gradually to 200 ml of boiling water, 20 ml of a 2% solution of ferric chloride. Red-brown ferric hydroxide sol is

produced by hydrolysis. When cold, free it from hydrochloric acid by dialysis.

(b) *Preparation of arsenious sulphide sol.* Boil about 1 g of arsenious oxide with 500 ml of water until all is dissolved, and allow to cool. (Crystalline arsenious oxide dissolves only very slowly; the amorphous form dissolves more rapidly.) Pass hydrogen sulphide, washed by bubbling through water, into the solution until the latter is saturated. Free the solution from excess of H_2S by means of a stream of hydrogen, and filter.

(c) *Electrophoresis.* Determine the sign of the charge on the sols by a U-tube moving-boundary apparatus (i.e. the inverse of the one used for emulsions—Fig. 14.6 (b)). By attaching a millimeter scale to the limb of the U-tube the rate at which the boundary moves can be determined, and knowing the voltage applied to the electrodes and their distance apart, the rate of movement for a potential gradient of 1 V per cm can be calculated.

Most hydrous oxide sols are positive, while metal sulphide sols are generally negative. However, it is possible to stabilize some sols (e.g. AgI) with either sign, by using a very slight excess of a salt of the cation or anion.

(d) *Mutual precipitation of colloids.* The mutual precipitation of colloids of opposite charge can be studied by mixing the sols together in various proportions. Mutual precipitation takes place only when the colloids are mixed together in certain proportions within rather narrow limits. When excess of one or other colloid is present precipitation does not occur or does so only incompletely.

Prepare sols of As_2S_3 and of dialyzed $Fe(OH)_3$, of 0·5% concentration (referred to As_2S_3 and Fe_2O_3 respectively). By means of graduated 10 ml pipettes mix in a series of test-tubes 1 ml As_2S_3 and 9 ml $Fe(OH)_3$; 3 ml As_2S_3 and 7 ml $Fe(OH)_3$, etc., and determine the relative concentrations at which complete precipitation occurs, and the supernatant liquid remains colourless after the mixtures have been allowed to stand for one or two hours.

In the above case the optimum amounts will be found to be about 9 ml As_2S_3 and 1 ml $Fe(OH)_3$. Vary the proportions by fractions of a millilitre on either side of the optimum point.

(e) *Precipitation of lyophobic colloids by electrolytes.* Lyophobic colloids are generally very sensitive to electrolytes; in some cases even quite small quantities of an electrolyte produce precipitation. The "precipitation value" or the concentration of an electrolyte necessary to cause precipitation depends on the nature of the colloid, on the method of its preparation, concentration, etc., as well as on the nature and valency of the electrolyte ions. In the

case of positively charged colloids the precipitation value depends on the valency of the electrolyte anion and is largely, although not entirely, independent of the nature of the cation; in the case of negatively charged colloids it is the valency of the cation that is of primary importance. The higher the valency, the lower is the precipitation value.

EXPERIMENT

Determine the precipitation values of NaCl, CaCl$_2$, *and* LaCl$_3$ *for arsenious sulphide sol.*

Prepare the sol of arsenious sulphide as described on p. 341, using a 0·5% solution of arsenious oxide. An approximate value of the precipitation concentration may be obtained by running from a burette, into a given volume (say, 50 ml) of the sol, solutions of known concentration of the different salts.

Having obtained approximate values for the precipitation concentrations, prepare solutions of the salts of appropriate concentration and proceed as indicated below.

(i) NaCl. Prepare a 0·2M solution of sodium chloride (11·7 g/litre), and from this prepare a series of 10 ml portions of diluted solution by mixing, in small test-tubes, 1, 3, 5, 7, 9 ml of NaCl solution with 9, 7, 5, 3, 1 ml of distilled water. In five test-tubes of as nearly as possible the same size, and well cleaned by steaming (p. 206), place 10 ml of the arsenious sulphide sol, and add to each of these in turn one of the five portions of diluted NaCl solution. After each addition mix well by inverting the tube two or three times, and then place in a rack for a definite time, say, one or two hours. At the end of this time ascertain in which cases precipitation has occurred, and so determine the concentration of NaCl necessary to produce precipitation.

In the above case, 1 ml of the original NaCl solution contains 0·0002 mole (or 0·2 millimole), and since this amount is then finally diluted to 20 ml, the concentration of the NaCl in the mixed solution will be 10 millimoles per litre; and in the other cases the concentration will be 30, 50, 70, 90 millimoles per litre. It will be found that in the case of the last two solutions, precipitation has taken place, but not in the case of the first two. In the case of the concentration 50 millimoles per litre, a turbidity will probably be observed. If necessary, further experiments with a concentration of 40 and 60 millimoles can be carried out in order to fix the value more closely.

(ii) CaCl$_2$. Proceed in the same way as for NaCl, starting with a 0·005M solution of CaCl$_2$ (0·555 g/litre). Dilute this in portions as above.

(iii) LaCl$_3$. Prepare a 0·005M solution of LaCl$_3$ (1·22 g/litre). For stock solution dilute this 10 times, and then dilute in portions as before.

Similar experiments can be carried out with ferric hydroxide sol. In this case use potassium chloride, sulphate, ferrocyanide, and ferricyanide as precipitating electrolytes.

(f) *Protective action of lyophilic colloids.* The precipitating action of electrolytes on lyophobic sols is diminished by the presence of lyophilic colloids (gelatin, albumin, starch, etc.); the latter are therefore said to exercise a *protective action.* To illustrate this, one may study the concentration of gelatin which will just prevent the precipitation of As_2S_3 by a certain definite concentration of electrolyte (e.g. NaCl). Solutions of gelatin are made up and by systematic dilution (as in the previous experiment) and mixing with a definite volume of As_2S_3 sol, one determines the concentration which just prevents precipitation when 1 ml of a 10% NaCl solution is added.

Lyophilic colloids. Lyophilic colloids comprise soluble macromolecules and aggregated molecules of smaller size. For obvious reasons they show the following characteristics of colloids: scattering of light (Faraday-Tyndall beam), low osmotic pressure, slow diffusion, electrophoresis (in the case of colloidal electrolytes), dialysis, high viscosity, reversibility (to drying), and, in some cases, moderate sensitivity to electrolytes.

(i) *Macromolecular colloids.* As an example of a wholly lyophilic colloid one may consider polystyrene in toluene. The polymer, like the monomer, is truly soluble in the "like-natured" solvent, but, because of its flexible, chain-like structure it causes a great increase of viscosity. The longer the chains, the greater the viscosity; this provides a method of determining the molecular weight of different polystyrenes. In a solvent of less favourable nature such as toluene–methanol mixtures, the chains become coiled instead of randomly extended, and the polymer has less influence on the viscosity. If a small proportion of the bifunctional monomer, divinyl benzene, is copolymerized with styrene one obtains a 3-dimensional polymer network. This cannot dissolve because of the *cross-links* which prevent unlimited extension, and the material behaves as a *gel* of definite *limited swelling* when placed in contact with the solvent.

Swelling gels can exert very large *swelling pressures*, but there is generally a slight *net contraction* when a gel imbibes solvent, especially in the case of the imbibition of water by materials containing hydrophilic groups. There is then an evolution of heat—*the heat of imbibition.*

Some supposedly typical lyophilic colloids become partially lyophobic if their electrical double layers are neutralized. For example, most proteins form stable solutions only in certain pH ranges; at their iso-electric point, or in the presence of large concentrations of simple salts or smaller concentrations of specific salts, they are precipitated just like lyophobic sols. It is evident

that proteins consist of a framework which is substantially hydrophobic, together with ionizable groups which, when dissociated, bestow a net hydrophilic nature. Partial removal of charge often produces *gels* in such materials; the structure is probably an open sponge-like, aggregate, "cross-linked" by weak secondary forces such as hydrogen bonds. Unlike the cross-linked polystyrene gels mentioned above, such gels are unstable, and show the phenomenon of *syneresis*, that is, a shrinkage with exudation of dilute colloidal solution.

Apart from osmometry[1] and electrophoresis,[2] the study of lyophilic colloids does not involve any special experimental techniques not already mentioned elsewhere. The qualitative phenomena can be studied with gelatin. This protein can be used to demonstrate (a) limited swelling in water at low temperatures, (b) swelling pressure, (c) heat of imbibition, (d) volume contraction on imbibition (by means of a dilatometer), (e) the influence of salt on gelation (Hofmeister series of ions), (f) syneresis of weak gels on standing, (g) non-Newtonian viscosity of solutions and ageing, (h) influence of salts on viscosity ("electro-viscous effect"), (i) effect of pH on viscosity and gelation, and (j) electrophoretic mobility (measured by microscopic observation of very small particles of quartz on which the protein is adsorbed).

(ii) *Aggregation colloids*. Solutions of soaps and synthetic detergents (the so-called "paraffin chain salts"), and also of many dyes, show colloidal properties such as anomalous osmotic pressure and diffusion rate and scattering of light. These solutions contain aggregates of colloidal size, known as *micelles*. At extremely low concentrations true crystalloidal solutions are formed, but, owing to the sharp onset of aggregation for a micelle containing many molecules (as shown by the Law of Mass Action), there is a fairly distinct concentration above which the solutions are almost entirely colloidal. This point is known as the *critical micelle concentration* (c.m.c.). At this point many properties of the solution, e.g. conductivity, f.p., surface tension, etc., show a change. Micelle formation is strongly favoured by addition of salts, since electrolytes reduce repulsion between ionized particles.

Solutions containing soap micelles exhibit the phenomenon of *solubilization*; this is the ability to dissolve appreciable quantities of substances which are practically insoluble in pure water, e.g. hydrocarbons, azobenzene. It is apparent that the substances are incorporated in the hydrophobic interior of the micelles. Solubilization shows a sharp increase above the c.m.c. By using certain dyes which exhibit a different colour when in solution in organic solvents from that shown in water, it is possible to determine the critical micelle concentration by a simple titration and to study the influence of salts and solubilized substances on this concentration.[3]

EXPERIMENT

Determine the influence of salts on the critical micelle concentration of a cationic soap.

Method. Prepare an approximately $10^{-5}M$ solution of pinacyanol chloride (or of Rhodamine 6G) in distilled water. To a measured volume of it add an accurately known quantity of a pure cationic soap, sufficient to change the colour to the shade typical of the solubilized dye. Then "titrate" this solution with the above dye solution until the change of shade is observed. Calculate the concentration of the soap at this point; this is the critical micelle concentration in the absence of salts. Suitable soaps are potassium laurate, potassium myristate, sodium cetyl sulphate, and their critical concentrations in water are about 2×10^{-2}, 6×10^{-3}, and $10^{-5}M$ respectively, showing that aggregation is favoured by increased chain length. It is necessary to have very pure samples of the compounds, otherwise an indistinct end-point is obtained.

Repeat the measurement, but with the previous addition of varied measured quantities of KCl, K_2SO_4, and $BaCl_2$.

Results. As with other colloid phenomena dependent on the electrical double layer, it is found that the number of charges on the ion having the same sign as the micelle has little influence, whereas micelle formation is more strongly favoured, with consequent lowering of the critical concentration, by polyvalent ions of sign *opposite* to that carried by the colloidal particles. This can be explained by a "closing-up" of the diffuse double layer by polyvalent gegenions.[4] In order to compare the effects of salts on different soaps it is found convenient to plot log (c.m.c.) against log (total gegenion concentration), a straight line being generally obtained.

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14C. RHEOLOGY OF COLLOIDS

One of the most common characteristics of many dispersions and materials of high molecular weight is their anomalous mechanical behaviour when subjected to deformation or flow. Rheology is the study of such phenomena. At present it is largely an empirical

science, lacking quantitative explanation in structural terms, but the rheological properties of colloids are often of great practical importance, as, for example, in the case of paints, creams, plastics, printing inks, and adhesives.

An *ideal solid*, when subjected to a *stress*, immediately assumes a deformation, such that the *strain* (e.g. extension) is proportional to the stress (Hooke's Law).   When the stress is removed the original form is exactly recovered.   Metals behave as ideal solids up to fairly high stresses, whereas most organic solids obey Hooke's Law only at very small stresses.

An *ideal liquid* ("Newtonian fluid") cannot withstand the smallest stress, but flows at a rate which is proportional to the applied stress (e.g. pressure): in other words, it shows a constant coefficient of viscosity (p. 87).   All pure, homogeneous, liquids are Newtonian, but colloidal solutions are generally non-Newtonian, especially when concentrated.

Suspensions, pastes, gels and emulsions frequently behave in a manner intermediate between that of a solid and a liquid.   For example, at *extremely* small stresses they may show recoverable, elastic deformation, and then, at slightly higher stresses, non-recoverable, time-dependent deformation, followed by flow (plasticity).   The flow may then increase proportionally with further increases of applied stress.   In other cases, the "pseudo-liquid" may show a "viscosity" which decreases with increasing rate of shear ("structural viscosity").   Some suspensions (e.g. bentonite paste) set to a gel when undisturbed, but temporarily liquefy when agitated ("thixotropy").   Long-chain polymers frequently give rise to *high elasticity*, as in rubber.   This is due to the tendency of the chains to assume a random-coiled distribution.   Solutions of chain-like molecules frequently show the property of being readily drawn out into threads ("Spinnbarkeit").

The phenomena mentioned above are a few of many rheological phenomena which may be encountered with colloids.   Because of their   technical   importance   instruments [1]   have been devised to measure many of them, although generally in relative rather than absolute terms.   For example, there is not yet any accepted absolute definition of thixotropy, but this property can readily be detected and studied by a rotating cylinder viscometer.   This instrument is probably the best for most kinds of "pseudo-fluids", but as an example of simple techniques which can be used to detect anomalous flow in colloidal solutions and suspensions a modified capillary viscometer may be mentioned.   The use of capillary methods is open to the criticism that the *rate of shear* is not uniform across the tube, and only a mean rate of shear can be stated; however, this

disadvantage is largely counter-balanced by the simplicity of the technique and by the fact that even with rotating cylinder viscometers the results cannot at present, be given quantitative interpretation.

In order to vary the rate of shear in a capillary viscometer, one uses an applied air pressure to drive the liquid instead of relying on gravity (as in the ordinary Ostwald viscometer, p. 89). The air pressure is measured on a manometer, and the rate of flow of the fluid is measured either by movement of a meniscus or by means of a sensitive gas flow-meter applied to the air displaced as the fluid moves.

Fig. 14.7 (a) shows the horizontal capillary viscometer used by Tsuda[2] for studying the structural viscosity of hydrophilic sols. Two lengths of tube, A and B, of equal, uniform bore, are separated by a length of capillary tube, C. Liquid is forced from A to B by an applied air pressure from a reservoir. The rate of flow is obtained
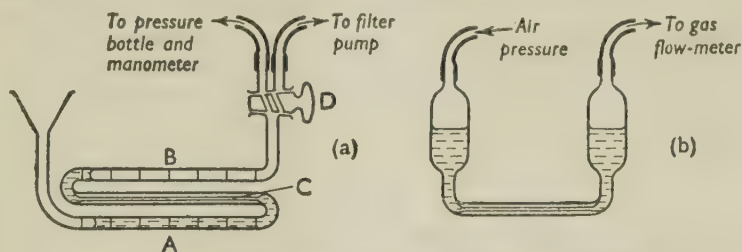
Fig. 14.7. Simple apparatus for study of non-Newtonian fluids.
(a) Tsuda's viscometer. (b) Capillary plastometer.

by timing the movement of the liquid meniscus as it passes marks on tubes A or B. Tubes A, B and C lie in the same horizontal plane.

Fig. 14.7 (b) shows a capillary tube "plastometer" suitable for studying more viscous suspensions and pastes[3]; the rate of flow can be measured by means of a 1 ml soap-bubble flow-meter (p. 83).

EXPERIMENT

*Determine the influence of applied pressure on the flow-rate of a 1%
starch sol.*

Procedure. Prepare a 1% starch solution by heating a starch paste on a water-bath for 1 hour; filter, if necessary. A viscometer of the form shown in Fig. 14.7 (a) is required. Its dimensions should be such that flow-times of about 10 to 100 seconds are obtained with water, using applied pressures of about 5 to 50 cm of water gauge; e.g. the capillary should be about 0·3 mm radius and 10 cm long, while A and B are of about 2.5 mm radius. A pipette to deliver a suitable quantity of liquid should be made.

Set the viscometer with its tubes horizontal in a water-bath or thermostat. Connect one arm of the 3-way tap D to a Winchester bottle (preferably immersed in a tank of water to eliminate temperature fluctuations) and to a long U-tube manometer. A side connection with stopcock must be provided for the purpose of pumping air into the bottle by means of a bicycle-pump with valve, and another stopcock is convenient for letting out air. The other arm of tap D is connected to a filter-pump. The pump is kept running. By turning D to the first position, the liquid in the viscometer can be pushed from B to A under a measured pressure; by reversing the tap connections, it can be drawn back again by the reduced pressure in readiness for a repetition of the measurement at the same or another pressure.

First make a series of measurements of the rate of flow with distilled water at a range of applied air pressures. The product of pressure × time of flow should remain constant so long as streamline flow is occurring. Avoid excessive flow-rates where this relation is found not to hold, as turbulence is then occurring.

Repeat the measurements with the same volume of starch solution.

Results. The *average* rate of shear β of a liquid flowing through a tube is given by

$$\beta = \frac{8}{3} \cdot \frac{V}{\pi r^3 t}$$

where V is the volume of liquid flowing in time t through a tube of radius r. The "specific viscosity" of a solute is defined by

$$\frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}} = \eta_{\text{sp}}$$

Plot η_{sp} against β. Wolfgang Ostwald found empirically that for many colloidal sols log (rate of flow) is a linear function of log (applied pressure).

Other experiments can be made with the same apparatus using solutions of methyl cellulose, gelatin, etc.; 0·5% agar solutions show a change of viscosity on standing for a few hours. Solutions of long-chain polymers in non-ionizing solvents, e.g. polystyrene in toluene, will be found to behave as Newtonian liquids in spite of their high η_{sp}. The apparatus shown in Fig. 14.7 (b) may be used to study plasticity in bentonite paste or a "solid" emulsion, (e.g. 50% medicinal paraffin-water, emulsified while heated with "self-emulsifying" glyceryl monostearate) or dilatancy with ground quartz suspensions.

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[3] Scott Blair and Crowther, *J. Phys. Chem.*, 1929, **33**, 321.

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APPENDIX 2

TABLE A1

MELTING POINTS, BOILING POINTS, DENSITIES AND REFRACTIVE INDICES OF SOME COMMON ORGANIC COMPOUNDS*

Compound	m.p.	b.p.	$\rho_4^{15°}$	$n_D^{15°}$
acetic acid	16·7	118·5	1·0515	1·3718 (20°)
acetone	− 94·6	56·3	0·7960	1·3616
iso-amyl acetate	—	142·0	0·8746 (20°)	1·4014 (18°)
n-amyl alcohol	− 73·8	138·3	0·8184	1·4117
iso-amyl alcohol	−117·2	131·6	0·8129	1·4084 (18°)
aniline	− 6·1	184·4	1·0261	1·5887
benzene	5·5	80·1	0·8842	1·5044
benzoic acid	122·4	250·0	—	—
bromobenzene	− 30·6	156·2	1·5017	1·5625
n-butyl alcohol	− 90	118·0	0·8134	1·4012
carbon disulphide	−112	46·3	1·2706	1·6317
carbon tetrachloride	− 22·9	76·8	1·6037	1·4631
chlorobenzene	− 45·2	132·0	1·1117	1·5275
chloroform	− 63·5	61·2	1·4985	1·4486
cyclo-hexane	6·4	80·8	0·7831	1·4289
p-dichlorobenzene	53·1	174		
ethyl acetate	− 82·4	77·1	0·9005 (20°)	1·3726 (20°)
ethyl alcohol	−114·6	78·3	0·7896 (20°)	1·3620 (20°)
ethyl bromide	−119	38·4	1·4708	1·4276
ethyl ether	−117	34·6	0·7193	1·3556
ethylene glycol	− 13	197·9	1·1171	1·4331
glycerol	18·1	290	1·2644	1·4732
n-hexane	− 95·0	68·8	0·6638	1·3779
methyl acetate	− 98·1	57·0	0·9337 (20°)	1·3614 (20°)
methyl alcohol	− 97·8	64·7	0·7952	1·3312
methyl bromide	− 93	4·5	—	—
naphthalene	80·1	217·7	—	—
nitrobenzene	5·7	210·8	1·2082	1·5546
n-pentane	−129·7	36·0	—	—
phenol	40·8	182·2	—	—
n-propyl alcohol	−127	97·2	0·8075	1·38
pyridine	− 41·8	115·5	0·9878	1·5124
tetrachloroethylene	− 22·4	121·1	1·6311	1·5057 (20°)
toluene	− 95·0	110·7	0·8716	1·4999
trichloroethylene	− 86·4	87	—	—
o-xylene	− 25·3	143	0·8804 (20°)	1·5037 (20°)
p-xylene	13·3	138·4	0·8654	1·4986

* Adapted from Partington, *Advanced Treatise of Physical Chemistry*, 1950, Vol. 1, Section VI A6 (Longmans, Green & Co, London).

TABLE A2

TRANSITION TEMPERATURES OF SOME SALT HYDRATES

Salts in equilibrium	° C*
$Na_2CrO_4.10H_2O + Na_2CrO_4.6H_2O$	19·53
$Na_2CrO_4.10H_2O + Na_2CrO_4.4H_2O$	19·99
$Na_2CrO_4.6H_2O \quad + Na_2CrO_4.4H_2O$	25·90
$Na_2CO_3.10H_2O \quad + Na_2CO_37H_2O$	32·02
$Na_2SO_4.10H_2O \quad + Na_2SO_4$	32·38
$NaBr.2H_2O \qquad + NaBr$	50·67
$MnCl_2.4H_2O \qquad + MnCl_2.2H_2O$	58·09
$SrCl_2.6H_2O \qquad + SrCl_2.2H_2O$	61·34

* Temperatures given are on the hydrogen scale. Mercury-in-glass thermometers give higher readings (cf. p. 39); the differences vary with the glass, and are about 0·05° at 10° C and 80° C, and about 0·1° between 30° and 60° C.

TABLE A3

EUTECTIC ("CRYOHYDRIC") TEMPERATURES OF SOME SALTS IN EQUILIBRIUM WITH ICE*

Salt	Eutectic temp. (° C)	Salt	Eutectic temp. (° C)
$Na_2SO_4.10H_2O$	− 1·10	$NaNO_2.\frac{1}{2}H_2O$	−19·5
$Na_2CO_3.10H_2O$	− 2·05	$NaCl.2H_2O$	−21·1
KNO_3	− 2·85	$NaBr.2H_2O$	−28
KCl	−10·65	$CaCl_2.6H_2O$	(−51)
KBr	−12·5		

* See Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, 3rd edn., 1940 (van Nostrand, New York).

TABLE A4

DENSITY OF WATER AT VARIOUS TEMPERATURES*

Temperature °C.	Density	Difference in density for 0·1°, in units of the sixth decimal place
0	0·999874	—
4	1·000000	0·8
5	0·999992	2·3
6	0·999969	3·8
7	0·999931	5·3
8	0·999878	6·6
9	0·999812	8·1
10	0·999731	9·4
11	0·999637	10·7
12	0·999530	12·0
13	0·999410	13·3
14	0·999277	14·5
15	0·999132	15·6
16	0·998976	16·8
17	0·998808	18·0
18	0·998628	19·1
19	0·998437	20·2
20	0·998235	21·2
21	0·998023	22·3
22	0·997800	23·2
23	0·997568	24·2
24	0·997326	25·3
25	0·997073	26·2
26	0·996811	27·1
27	0·996540	28·0
28	0·996260	29·0
29	0·995971	29·7
30	0·995674	—

* See also Table 2.2 (p. 31) giving the apparent specific wt. and specific vol. of water in air.

TABLE A5

VAPOUR PRESSURE OF WATER AT VARIOUS TEMPERATURES

° C	0	2	4	5	6	8
0	4·6	5·3	6·1	6·5	7·0	8·0
10	9·2	10·5	12·0	12·8	13·6	15·5
20	17·5	19·8	22·3	23·7	25·1	28·3
30	31·7	35·5	39·8	42·0	44·4	49·5

40°	55·2	60°	149·3	80°	355·1
45°	71·8	65°	187·4	85°	433·6
50°	92·4	70°	233·6	90°	525·8
55°	117·9	75°	289·0	95°	633·9

TABLE A6

TEMPERATURE—E.M.F. TABLES FOR THERMOCOUPLES

Temperature ° C	Copper-constantan	Chromel-alumel	Platinum/ 13% rhodium-platinum*
−200	−5·54	−5·75	—
−100	−3·35	−3·49	—
0	0	0	0
10	0·39	0·40	0.054
20	0·79	0·80	0·111
30	1·19	1·20	0·170
40	1·61	1·61	0·231
50	2·03	2·02	0·295
100	4·28	4·10	0·644
200	9·29	8·13	1·463
300	14·86	12·21	2·392
400	20·87	16·39	3·397
500	—	20·64	4·460
600	—	24·90	5·571
700	—	29·14	6·735
800	—	33·31	7·952
900	—	37·36	9·209
1,000	—	41·31	10·510
1,200	—	—	13·222
1,400	—	—	16·039
1,600	—	—	18·855

* After Barber *Proc. Phys. Soc.*, 1950, **63**, 492.

The tables give the e.m.f. (in millivolts) generated by a thermocouple with one junction at 0° C and the other at the temperature shown.   Interpolation may be linear.   For accurate work reliance should not be placed on the tables (except with platinum thermocouples), but individual couples should be calibrated at fixed temperatures (see Table 3.1).

TABLE A7

SALTS FOR CONTROLLING RELATIVE HUMIDITY AT 25° C*

The table gives the relative humidity (i.e. v.p. of solution/v.p. of water $\times 100$) for *saturated* solutions of the salts.

Salt	r.h.	Salt	r.h.
$NaOH.H_2O$	7·0	$SrCl_2.6H_2O$	70·8
$LiCl.H_2O$	11·1	$NaNO_3$	73·7
$K(C_2H_3O_2).1·5 H_2O$	22·5	$NaCl$	75·3
$MgCl_2.6H_2O$	33·0	KBr	80·7
$K_2CO_3.2H_2O$	42·8	KCl	84·3
$LiNO_3.3H_2O$	47·1	$BaCl_2.2H_2O$	90·2
$Mg(NO_3)_2.6H_2O$	52·9	KNO_3	92·5
$NaBr.2H_2O$	57·7	$K_2Cr_2O_7$	98·0

* Stokes and Robinson, *Ind. Eng. Chem.*, 1949, **41**, 2013.

TABLE A8

SHORT LIST OF PROMINENT SPECTRAL LINES IN THE VISIBLE REGION*

Flame spectra

barium	boric acid	calcium	caesium	lithium
5137	5193	4227	4555p	6104
5347	5440	5544	4593p	6708
5535p	5481	6182p	6213	
		6203p	6723	
			6973	

potassium	rubidium	sodium	strontium	thallium
4044	4202p	5890p	4078	5350
4047	4216p	5896p	4608	
7668p	6299		6060	
7699p	7800		6387	
	7948		6628	

Spectra of electric arcs or discharges

argon	cadmium	copper	helium	hydrogen	mercury	neon
4159	4678	4023	3889	4102	4047	6143
4192	4800	4063	4471	4340	4078	6267
4198	5086	4587	5876	4861	4358	6383
4201	6348	5106		6563	5461	6402
4259		5153			5770	6507
4703		5218			5791	
6031		5700			6908	
		5782				

* Wavelengths in Ångstrom units: p marks particularly "persistent" line. See Bibliography 8B (p. 159) for sources of more detailed tables.

TABLE A9

SOLUBILITIES OF SOME SPARINGLY-SOLUBLE SALTS AT $25°$ C*

Solubilities are given in g per litre.

Salt	Solubility	Salt	Solubility
lead chloride	10·8	silver chromate	0·029
lead iodide	0·76	silver bromide	0·00014
lead sulphate	0·045	silver thiocyanate	0·00017
silver benzoate	2·61	thallous chloride	3·85
silver chloride	0·00195		

* See Seidell, *Solubility of Inorganic and Metal Organic Compounds*, 3rd. edn., 1940 (van Nostrand, New York).

TABLE A10

MEAN ION ACTIVITY COEFFICIENT OF SOME COMMON ELECTROLYTES AT 25° C

Valence type	Electrolyte	molality			
		0·001	0·01	0·1	1
1 : 1	HCl	0·965	0·904	0·796	0·809
	HNO₃	0·96	0·90	0·79	0·72
	LiCl	0·96	0·90	0·79	0·77
	KCl	0·965	0·902	0·771	0·611
	KOH	0·96	0·90	0·80	0·76
	KNO₃	0·965	0·896	0·723	0·44
	AgNO₃	0·96	0·892	0·733	0·43
	*	0·966	0·901	0·758	0·55
1 : 2	BaCl₂	0·88	0·72	0·50	0·39
	H₂SO₄	0·84	0·54	0·38	0·19
	**	0·89	0·72	0·44	0·21
1 : 3	LaCl₃	0·85	0·64	0·31	0·34
2 : 2	CuSO₄	0·74	0·41	0··15	0·04
2 : 3	La₂(SO₄)₃	—	—	0·04	0·02

*, ** Average behaviour of 1 : 1 and 1 : 2 electrolytes; see Güntelberg formula, p. 343.

For further data see Landoft-Bornstein table; and Stokes and Robinson, *Trans. Faraday Soc.*, 1949, **45**, 612.

TABLE A11

REDUCTION OF BAROMETRIC READINGS TO 0° C

When the barometer has a brass scale, the corrected barometric height B_0 is given by the expression,

$$B_0 = B\left[1 - \frac{(\beta - \alpha)t}{(1 + \beta t)}\right]$$

where B and t are the observed height and temperature; $\alpha = 0.0000184$, the coefficient of linear expansion of brass; $\beta = 0.0001818$, the coefficient of cubical expansion of mercury.

In the following table are given the corrections in millimetres to be *subtracted* from the observed barometric height.

Temp.	Barometric readings			
	720.	740.	760.	780.
10°	1·17	1·21	1·24	1·27
12°	1·41	1·45	1·49	1·53
14°	1·64	1·69	1·73	1·78
16°	1·88	1·93	1·98	2·03
18°	2·11	2·17	2·23	2·29
20°	2·34	2·41	2·47	2·54
22°	2·58	2·65	2·72	2·79
24°	2·81	2·89	2·97	3·05
26°	3·04	3·13	3·21	3·30
28°	3·28	3·37	3·46	3·55
30°	3·51	3·61	3·71	3·80

TABLE A12

REDUCTION OF BAROMETRIC READINGS TO LATITUDE 45° AND SEA-LEVEL

In the following table are given the corrections (C) in millimetres to reduce the barometric readings, corrected for temperature, to the values at latitude 45°. In latitudes between 0° and 45°, the corrections must be subtracted, and in latitudes between 45° and 90°, they must be added.

Latitude	0° 90°	5° 85°	10° 80°	15° 75°	20° 70°	25° 65°	30° 60°	35° 55°	40° 50°	45° 45°
C	1·97	1·94	1·85	1·70	1·51	1·27	0·98	0·67	0·34	0·00

For each 1,000 metres above sea-level, 0·24 mm must be subtracted from the observed reading.

TABLE A13

IONIC CONDUCTIVITIES AT INFINITE DILUTION

Cation	18°	25°	Anion	18°	25°
Ag^+	54·3	63·5	Br^-	67·2	77·4
H^+	314	350	Cl^-	65·5	75·5
K^+	64·6	74·5	I^-	66·4	76·2
Na^+	43·5	50·9	NO_3^-	61·7	70·6
NH_4^+	64	73·9	OH^-	172	192
$\frac{1}{2}Ba^{++}$	55	65	Ac^-	35	40·8
$\frac{1}{2}Ca^{++}$	51	60	$\frac{1}{2}C_2O_4^{--}$	63	73
$\frac{1}{2}Pb^{++}$	61·5	72·0	$\frac{1}{2}SO_4^{--}$	68	79
$\frac{1}{2}Mg^{++}$	45	53·1	$\frac{1}{2}CrO_4^{--}$	72	83·6 (?)

TABLE A14

VISCOSITIES OF LIQUIDS IN MILLIPOISES

Substance	0°	10°	20°	30°	40°	50°
aniline	122·0	64·5	42·7	31·1	23·6	18·6
alcohol, methyl	8·08	6·90	5·93	5·15	4·49	3·95
,, ethyl	17·72	14·66	12·00	10·03	8·34	7·02
benzene	9·00	7·57	6·47	5·61	4·92	4·36
carbon tetrachloride	13·51	11·38	9·75	8·48	7·46	6·62
chloroform	6·99	6·25	5·63	5·10	4·64	4·24
toluene	7·72	6·71	5·90	5·25	4·71	4·26
water	17·938	13·097	10·087	8·004	6·536	5·492

TABLE A15

SURFACE TENSION OF LIQUIDS

Substance	Surface tension in dynes per centimetre at					
	0°	10°	20°	30°	40°	50°
water	75·64	74·22	72·75	71·18	69·56	67·91
ethyl alcohol	24·05	23·14	22·27	21·43	20·60	19·80
ethyl acetate	26·5	—	23·9	—	—	20·2
carbon tetrachloride	—	28·00	26·77	25·53	—	23·14
ethyl ether	—	—	17·01	—	—	13·47
benzene	31·58	30·22	28·88	27·56	26·26	24·98

INDEX

N.B. *Entries in bold type refer to sections—see heads of pages.*

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	26	30	34	38
											4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	15	19	23	27	31	35
											4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	14	18	21	25	28	32
											3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	13	16	20	23	26	30
											3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	28
											3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	9	11	14	17	20	23	26
											3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	14	16	19	22	24
											3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	13	15	18	20	23
											2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
											2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
											2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4